

Quantum Statistical Mechanics. II. Stochastic Schrödinger Equation

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The stochastic dissipative Schrödinger equation is derived for an open quantum system consisting of a sub-system able to exchange energy with a thermal reservoir. The resultant evolution of the wave function also gives the evolution of the density matrix, which is an explicit, stochastic form of the Lindblad master equation. A quantum fluctuation-dissipation theorem is also derived. The time correlation function is discussed.

I. INTRODUCTION

Quantum mechanics is often portrayed as synonymous with randomness and unpredictability, as opposed to the deterministic nature of the classical world. However this distinction is overly simplistic since Schrödinger's equation is completely deterministic and it gives the evolution of the wave function of an isolated system with complete certainty. Conversely the classical evolution of a sub-system that can exchange energy with a thermal reservoir has a random character such that the future can only be predicted from the present state of the sub-system with statistical probability rather than deterministic certainty.^{1,2} In this latter case Hamilton's equations of motion for the isolated system must be augmented with dissipative and stochastic terms that arise from the probabilistic treatment of the reservoir.^{2,3} This raises the question of whether one might similarly modify Schrödinger's equation in the quantum case in order to incorporate the reservoir environment probabilistically.

The main result obtained in the present paper is the stochastic dissipative Schrödinger equation for a sub-system able to exchange energy with a thermal reservoir. This is a direct analogue of the stochastic dissipative Hamilton's equation that has recently been derived for classical equilibrium statistical mechanics.^{2,3} The stochastic dissipative Schrödinger equation derived here provides a new way to treat equilibrium quantum systems. One possible application is as a thermostat for computer simulation algorithms for quantum statistical mechanics. In addition, since it gives the evolution of an open quantum system, it will likely play a role in the development of a theory for non-equilibrium quantum statistical mechanics.

The origin of the stochastic Schrödinger equation in the present formulation of quantum statistical mechanics differs from the literature (e.g. Refs [4–10]). Also called Belavkin equations, stochastic Schrödinger equations conventionally describe the evolution of the quantum state of a continuously measured system. In this interpretation, the stochastic character of the quantum trajectories result from the measurement process.

A second, related field of study concerns quantum dissipative systems, which modify the Schrödinger equation with Langevin-type dissipative and fluctuation terms.^{11,12} This approach is related to that taken here in that it deals with an open quantum system with the extra

terms accounting for the interactions with the reservoir beyond the sub-system of direct interest. In the literature one finds three main approaches:¹² modification of the procedure of quantization, such as using complex variables, or a non-linear Schrödinger equation,^{13–16} the postulation of a heuristic stochastic form of the Schrödinger equation,^{6,11,17,18} and the projection from the reservoir onto the sub-system of the density matrix,^{19,20} or operator.^{21,22} In the projection category one can note the quantum Langevin equation,^{23,24} which can be derived from an harmonic oscillator bath with linear coupling, the so-called Caldeira-Leggett model.²⁵

The stochastic Schrödinger equation developed here also arises from the projection of the reservoir onto the sub-system. Here the emphasis on the statistical origin of the equation and the exact symmetry requirements that the equation must obey. The derivation follows closely that given in the classical case of the stochastic Hamilton's equations of motion.^{2,3} The present equation allows the computation of the time evolution of the wave function of a sub-system of a thermal reservoir, with the reservoir accounted for in a macroscopic probabilistic sense. The stochastic and deterministic terms that arise are shown to be related by a quantum fluctuation-dissipation theorem.

II. STATIC PROPERTIES

A. Background

In Paper I,²⁶ two results were established that provide the starting point for the present paper. For a canonical equilibrium system (i.e. a sub-system that can exchange energy with a thermal reservoir of temperature T), it was shown that the probability operator had Maxwell-Boltzmann form

$$\hat{\rho} = \frac{1}{Z(T)} e^{-\hat{\mathcal{H}}/k_B T}. \quad (2.1)$$

Here $\hat{\mathcal{H}}$ is the Hamiltonian or energy operator of the sub-system and k_B is Boltzmann's constant. This result is the same as the conventional expression that is postulated for the canonical quantum probability operator.^{27–30}

For future reference the entropy operator is $\hat{S} = -\hat{\mathcal{H}}/T$. The normalized energy eigenfunctions ζ_n^E , $\hat{\mathcal{H}}|\zeta_n^E\rangle = E_n|\zeta_n^E\rangle$, are also entropy eigenfunctions, $\zeta_n^S =$

$\zeta_n^E, \hat{S}|\zeta_n^S\rangle = S_n|\zeta_n^S\rangle$, with $S_n \equiv S_{nn}^S = -E_n/T$. Here the degeneracy is not shown explicitly.

The second result invoked here from Paper I²⁶ is that the statistical average of an operator has the conventional von Neumann form,^{27–30}

$$\langle \hat{O} \rangle_{\text{stat}} = \text{Tr } \hat{\wp} \hat{O}. \quad (2.2)$$

These two results followed from the conservation law for energy, which implied that the sub-system wave function and the reservoir wave function are entangled.²⁶ This in turn implied that the principle energy quantum states collapsed. The degenerate reservoir energy quantum states were shown to sum to give the Maxwell-Boltzmann form for the probability operator. Whilst superposition states with a given energy can be composed from the degenerate sub-system energy quantum states, it was shown that these cancel and that there is no contribution to the statistical average of an operator from the non-diagonal terms in the energy representation. Since the statistical average contains only diagonal terms in either the energy or the operator representation, it may be interpreted as resulting from the collapse of the wave function (c.f. Eqs (2.6) and (2.7) below).

The goal of this paper is to derive a stochastic dissipative form of the Schrödinger equation that represents the evolution of the wave function of the sub-system in the presence of the reservoir. Accordingly an expression will be required for the average of an operator that invokes the resultant wave function and its trajectory. The focus is less on pure quantum states, as in the von Neumann expression, Eq. (2.2), and more on expressing the average as an expectation value of a wave function state.

Toward this end, and to illustrate the underlying philosophy of the present approach, it is now shown that the von Neumann statistical average, Eq. (2.2), can be written as an integral of an expectation value over wave space. Making an expansion in entropy eigenfunctions, one has

$$\begin{aligned} & \int d\psi \frac{\langle \psi | \hat{\wp} \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \int d\psi^S \frac{1}{N(\psi)} \sum_{lmn} \psi_l^{S*} \psi_n^S \wp_{lm}^S O_{mn}^S \\ &= \sum_{mn} \wp_{mm}^S O_{mn}^S \int d\psi^S \frac{1}{N(\psi)} \psi_m^{S*} \psi_n^S \\ &= \sum_n \wp_{nn}^S O_{nn}^S \int d\psi^S \frac{1}{N(\psi)} \psi_n^{S*} \psi_n^S \\ &= \text{const.} \sum_{mn} \wp_{mn}^S O_{nm}^S \\ &= \text{Tr } \hat{\wp} \hat{O}. \end{aligned} \quad (2.3)$$

The third equality follows because the integrand for the terms $m \neq n$ is odd, and so they vanish upon integration. The fourth equality follows because the value of the integral does not depend on n , and because

$\wp_{mn}^S = \wp_{nn}^S \delta_{mn}$. The constant is incorporated into the normalization factor.

Continuing the focus on wave space, one can explore the possible utility of a probability density. For the present canonical equilibrium case, for which the Maxwell-Boltzmann distribution holds, there are two plausible definitions namely

$$\wp(\psi) = \frac{1}{Z(T)} \frac{\langle \psi | e^{-\hat{\mathcal{H}}/k_B T} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (2.4)$$

or

$$\tilde{\wp}(\psi) = \frac{1}{Z(T)} e^{-E(\psi)/k_B T}, \quad E(\psi) = \frac{\langle \psi | \hat{\mathcal{H}} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.5)$$

These differ if the system is in a superposition of entropy states. However if the system has collapsed into a pure entropy eigenstate, then these are equal ($\wp(\zeta_{ag}^S) = \tilde{\wp}(\zeta_{ag}^S) = Z(T)^{-1} e^{-E_{\alpha}/k_B T}$). Neither probability density gives the statistical average of an operator as an integral over wave space

$$\langle \hat{O} \rangle_{\text{stat}} \neq \int d\psi \wp(\psi) O(\psi), \quad (2.6)$$

where the expectation value of the operator is $O(\psi) = \langle \psi | \hat{O} | \psi \rangle / \langle \psi | \psi \rangle$. The reason that this fails is that this expression always contains contributions from the superposition states and never reduces to a sum over pure quantum states of either the observable operator or of the entropy operator.

However, the collapse of the wave function into entropy eigenstates yields

$$\begin{aligned} \langle \hat{O} \rangle_{\text{stat}} &= \int_{\text{coll.}} d\psi \wp(\psi) O(\psi) \\ &= \sum_n \wp(\zeta_n^S) O(\zeta_n^S) \\ &= \frac{1}{Z(T)} \sum_n e^{-E_n/k_B T} O_{nn}^S \\ &= \text{Tr } \hat{\wp} \hat{O}. \end{aligned} \quad (2.7)$$

Whereas $\wp(\psi)$ gives directly the operator $\hat{\wp}$ and so the von Neumann trace form, the density $\tilde{\wp}(\psi)$ does not directly give a probability operator and the average cannot be written as a trace over operators (but it can be written as a sum over entropy states of this probability density). The ‘correct’ probability density is related to the ‘correct’ or actual entropy, $\wp(\psi) = Z(T)^{-1} \exp S_r(\psi)/k_B$, where the entropy is $S_r(\psi) = k_B \ln \langle \psi | e^{\hat{S}_r/k_B} | \psi \rangle / \langle \psi | \psi \rangle$, whereas the ‘incorrect’ probability density is related to the expectation entropy, $\tilde{\wp}(\psi) = Z(T)^{-1} \exp S_r^{<>}(\psi)/k_B$, where $S_r^{<>}(\psi) = \langle \psi | \hat{S}_r | \psi \rangle / \langle \psi | \psi \rangle$.³¹

The main focus of the present paper is on the stochastic, dissipative Schrödinger equation and the trajectory that it generates through wave space. Accordingly, the

relationship between the above expressions for the statistical average and an expression based upon the time average over the trajectory is now discussed.

An obvious requirement for an equilibrium system is that the probability operator be stationary. With $\hat{U}(t', t)$ the appropriate stochastic, dissipative propagator, one must have

$$\hat{\rho} = \left\langle \hat{U}(t', t)^\dagger \hat{\rho} \hat{U}(t', t) \right\rangle_{\text{stoch}}, \quad (2.8)$$

where the Maxwell-Boltzmann operator appears on both sides. This is a formal requirement for the time evolution of the *equilibrium* probability operator.

The stochastic, dissipative propagator can also be used to generate a trajectory in wave space,

$$|\psi(t')\rangle \equiv |\psi(t'|\psi, t)\rangle = \hat{U}(t', t) |\psi\rangle. \quad (2.9)$$

In view of the stationarity of the probability operator with respect to the propagator, one might suppose that this trajectory samples wave space in proportion to the probability density. Such a supposition is only partially correct, as is discussed in the text.

With a single wave function, one can only make a superposition of states, not a mixture of states. So even if the wave function was composed of entropy modes with the correct entropy weight, $|\psi\rangle = \sum_n e^{S_n/2k_B} |\zeta_n^S\rangle$, the density matrix formed from it would not equal the probability operator,

$$|\psi\rangle\langle\psi| = \frac{1}{Z(T)} \sum_{nm} e^{[S_m+S_n]/2k_B} |\zeta_m^S\rangle\langle\zeta_n^S| \neq \hat{\rho}. \quad (2.10)$$

(The probability operator is of course diagonal in the entropy representation.)

One can nevertheless use a density matrix of the wave function provided that the superposition states average to zero over the trajectory. If the wave function evolves without mixing modes,

$$\psi_m^S(t') = e^{i\phi_m t'} \psi_m^S(0). \quad (2.11)$$

then the time average of the density matrix is

$$\begin{aligned} & \frac{1}{t} \int_0^t dt' |\psi(t')\rangle\langle\psi(t')| \\ &= \frac{1}{t} \int_0^t dt' \sum_{mn} \psi_m^S(t') \psi_n^S(t')^* |\zeta_m^S\rangle\langle\zeta_n^S| \\ &= \sum_{mn} \psi_m^S(0) \psi_n^S(0)^* |\zeta_m^S\rangle\langle\zeta_n^S| \\ & \quad \times \frac{1}{t} \int_0^t dt' e^{i(\phi_m - \phi_n)t'} \\ &= \sum_m \psi_m^S(0) \psi_m^S(0)^* |\zeta_m^S\rangle\langle\zeta_m^S|. \end{aligned} \quad (2.12)$$

The off-diagonal phase factors average to zero. This corresponds to a statistical mixture. So if the initial coefficients are distributed according to the exponential of

the entropy, $\psi_m^S(0) \propto e^{S_m/2k_B}$, one will get the correct canonical equilibrium probability operator as the time average of the density matrix,

$$\hat{\rho} = \frac{1}{t} \int_0^t dt' \frac{1}{N(\psi(t'))} |\psi(t')\rangle\langle\psi(t')|. \quad (2.13)$$

Here and below, $N(\psi) \equiv \langle\psi|\psi\rangle$ is the norm.

The same result will hold when the wave function mixes entropy modes as it evolves, since the phase factors of the modes are random. This case is the most powerful application of the stochastic, dissipative Schrödinger equation discussed in the text since with it the density matrix converges over the trajectory to the equilibrium probability operator from an arbitrary starting wave function.

From this follows the fourth form for the statistical average: it is a time average of the expectation value over the stochastic trajectory,

$$\begin{aligned} \langle\hat{O}\rangle_{\text{stat}} &= \text{Tr } \hat{\rho} \hat{O} \\ &= \sum_{mn} \langle\zeta_m|\hat{\rho}|\zeta_n\rangle \langle\zeta_n|\hat{O}|\zeta_m\rangle \\ &= \frac{1}{t} \int_0^t dt' \sum_{mn} \frac{\langle\zeta_m|\psi(t')\rangle \langle\psi(t')|\zeta_n\rangle O_{nm}}{N(\psi(t'))} \\ &= \frac{1}{t} \int_0^t dt' \sum_{mn} \frac{\psi_m(t') \psi_n(t')^* O_{nm}}{N(\psi(t'))} \\ &= \frac{1}{t} \int_0^t dt' \frac{\langle\psi(t')|\hat{O}|\psi(t')\rangle}{\langle\psi(t')|\psi(t')\rangle}. \end{aligned} \quad (2.14)$$

The final equality has the appearance that superposition states contribute to the average, but the first equality makes it clear that these must average to zero.

A direct consequence of the density matrix averaged over the stochastic trajectory equalling the probability operator, Eq. (2.13), is that different entropy modes are uncorrelated,

$$\frac{1}{t} \int_0^t dt' \frac{\psi_m^S(t') \psi_n^S(t')^*}{N(\psi(t'))} = \delta_{mn} \varphi_{mm}^S. \quad (2.15)$$

This reduces the average to a single sum in the entropy basis, as it must.

B. First Entropy

1. Definition

In the classical case, the exponential of the entropy is essentially the probability.^{1,2} A similar definition may be invoked in the quantum case for the entropy operator,

$$\hat{\rho} = \frac{1}{Z} e^{\hat{S}/k_B}, \quad (2.16)$$

where k_B is Boltzmann's constant. In view of the form of the Maxwell-Boltzmann probability operator, Eq. (2.1),

one can identify the entropy operator for the canonical equilibrium system as

$$\hat{S} = \frac{-1}{T} \hat{\mathcal{H}}. \quad (2.17)$$

(Logically, the entropy operator is first derived, and the Maxwell-Boltzmann form for the probability follows.)²⁶

The expectation value of the reservoir entropy (expectation entropy, for short) is

$$S_r^{<>}(\psi) \equiv \frac{\langle \psi | \hat{S} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{-1}{T} \frac{\langle \psi | \hat{\mathcal{H}} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.18)$$

The actual entropy is

$$S_r(\psi) = k_B \ln \frac{\langle \psi | e^{\hat{S}/k_B} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.19)$$

This gives the reservoir entropy for the given wave state of the sub-system. This is the same as the total entropy, $S_{\text{tot}}(\psi) \equiv S_r(\psi) + S_s(\psi) = S_r(\psi)$, since the sub-system entropy of a wave state vanishes (see Appendix B of Ref. 26).

As mentioned above, the ‘correct’ probability density is related to the ‘correct’ or actual entropy, $\wp(\psi) = Z(T)^{-1} \exp S(\psi)/k_B$, whereas the ‘incorrect’ probability density is related to the expectation entropy, $\tilde{\wp}(\psi) = Z(T)^{-1} \exp S^{<>}(\psi)/k_B$.

The projection of the wave function onto the entropy ground state is denoted $|\bar{\psi}\rangle = \hat{\mathcal{P}}_0|\psi\rangle = \sum_g |\zeta_{0g}^S\rangle \langle \zeta_{0g}^S | \psi \rangle$. The maximum value of the entropy occurs in the ground state value, and it is denoted $S_0 \equiv S_r(\bar{\psi}) \equiv \bar{S}_r$. In this sense this can be called the most likely wave state, although such a designation is a little misleading because it is not a unique wave state but rather the projection of the current wave state onto the most likely sub-space.

2. Derivatives

The thermodynamic force is

$$\begin{aligned} \hat{S}'_r(\psi) | \psi \rangle &\equiv \frac{\partial S_r(\psi)}{\partial \langle \psi |} \\ &= \frac{k_B}{N(\psi)} \left[\frac{e^{\hat{S}_r/k_B}}{e^{S_r(\psi)/k_B}} - \hat{\mathbf{I}} \right] | \psi \rangle. \end{aligned} \quad (2.20)$$

This defines the entropy force operator, $\hat{S}'_r(\psi)$, which, because it depends upon the wave state, is a non-linear operator.

The second derivative gives the entropy fluctuation operator,

$$\begin{aligned} \hat{S}''_r(\psi) &\equiv \frac{\partial S_r(\psi)}{\partial \langle \psi | \partial \langle \psi |} \\ &= k_B \left[\frac{e^{\hat{S}_r/k_B}}{\langle \psi | e^{\hat{S}_r/k_B} | \psi \rangle} - \frac{1}{\langle \psi | \psi \rangle} \hat{\mathbf{I}} \right] \\ &\quad - k_B \frac{e^{\hat{S}_r/k_B} | \psi \rangle \langle \psi | e^{\hat{S}_r/k_B}}{\langle \psi | e^{\hat{S}_r/k_B} | \psi \rangle^2} + k_B \frac{| \psi \rangle \langle \psi |}{\langle \psi | \psi \rangle^2}. \end{aligned} \quad (2.21)$$

This is also a non-linear operator.

When the entropy fluctuation operator is evaluated in the entropy ground state the final two terms cancel, so that it is equal to the thermodynamic force operator,

$$\hat{S}''_r(\bar{\psi}) = \hat{S}'_r(\bar{\psi}) = \frac{k_B}{N(\bar{\psi})} \left[\frac{e^{\hat{S}_r/k_B}}{e^{S_0/k_B}} - \hat{\mathbf{I}} \right]. \quad (2.22)$$

These will also be denoted $\hat{S}''_r = \hat{S}'_r$. The non-linearity means that effectively the entropy gradient decreases in magnitude with increasing projection of the wave function onto the ground state. By design, the thermodynamic force vanishes in the most likely wave state, $\hat{S}''_r(\bar{\psi}) = \hat{S}'_r(\bar{\psi}) = |0\rangle$. Further, the fluctuation operator is negative semi-definite, $\langle \psi | \hat{S}''_r | \psi \rangle \leq 0$.

3. Fluctuation Form

As mentioned above, the total entropy is given by

$$e^{S(\psi|T)/k_B} = \frac{\langle \psi | e^{\hat{S}_r/k_B} | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.23)$$

In the canonical equilibrium case the entropy operator is $\hat{S}_r = -\hat{\mathcal{H}}/T$.

One may define the fluctuation of a wave function as its departure from the most likely value, $\Delta\psi \equiv \psi - \bar{\psi}$. In terms of this, one carries out a second order expansion about the most likely wave function and writes the first entropy in fluctuation approximation as

$$S_r(\psi) = \bar{S}_r + \langle \Delta\psi | \hat{S}''_r | \Delta\psi \rangle + \mathcal{O}(\Delta\psi^3), \quad (2.24)$$

where the value in the most likely state is $\bar{S}_r \equiv S_r(\bar{\psi}) = S_0 = -E_0/T$. As mentioned, because the most likely state maximizes the first entropy, the entropy fluctuation operator is negative semi-definite.

Since $\hat{S}''_r = \hat{S}'_r$, differentiating the fluctuation form gives the thermodynamic force as $\partial S_r(\psi)/\partial \langle \psi | = \hat{S}''_r | \Delta\psi \rangle + \mathcal{O}(\Delta\psi^2)$. One could replace in this $\hat{S}''_r \Rightarrow \hat{S}'_r(\psi)$, or $|\Delta\psi\rangle \Rightarrow |\psi\rangle$, or both, without changing the leading order in the fluctuation expansion. However, in this case the fluctuation operator is no longer negative semi-definite, which is a disadvantage.

C. Helmholtz Free Energy

The total unconstrained entropy is the logarithm of the partition function, and it may be rewritten as

$$\begin{aligned} S_{\text{tot}}(T) &= k_B \ln Z(T) \\ &= k_B \text{Tr} \{ \hat{\wp}(T) \ln Z(T) \} \\ &= k_B \text{Tr} \left\{ \hat{\wp}(T) \left[-\ln \hat{\wp}(T) + \ln e^{-\hat{\mathcal{H}}/k_B T} \right] \right\} \\ &= \frac{-1}{T} \text{Tr} \left\{ \hat{\wp}(T) \hat{\mathcal{H}} \right\} \\ &\quad - k_B \text{Tr} \{ \hat{\wp}(T) \ln \hat{\wp}(T) \}. \end{aligned} \quad (2.25)$$

This is written in the form of a sum over quantum states. It can be equivalently written as an integral over the Hilbert space,

$$\begin{aligned}
S_{\text{tot}}(T) &= k_B \ln Z(T) \\
&= k_B \int d\psi \frac{\langle \psi | \hat{\rho}(T) \ln Z(T) | \psi \rangle}{\langle \psi | \psi \rangle} \\
&= k_B \int d\psi \left[\frac{-\langle \psi | \hat{\rho}(T) \ln \hat{\rho}(T) | \psi \rangle}{\langle \psi | \psi \rangle} \right. \\
&\quad \left. + \frac{\langle \psi | \hat{\rho}(T) \ln e^{-\hat{H}/k_B T} | \psi \rangle}{\langle \psi | \psi \rangle} \right] \\
&= \frac{-\langle \hat{H} \rangle_T}{T} - k_B \int d\psi \frac{\langle \psi | \hat{\rho}(T) \ln \hat{\rho}(T) | \psi \rangle}{\langle \psi | \psi \rangle}.
\end{aligned} \tag{2.26}$$

The equivalence of these expressions follows from the collapse of the wave function, Eq. (2.3): the trace can be formulated equivalently as a sum over quantum states or as an integral over Hilbert space.

The first term is evidently the unconstrained reservoir entropy (c.f. Eq. (2.17), averaged over the sub-system microstates),

$$S_r(T) = \frac{-1}{T} \langle \hat{H} \rangle_T. \tag{2.27}$$

This is the average of wave space of the expectation entropy. In so far as the wave function has collapsed into entropy eigenstates, the latter is the same as the actual entropy.

Because the probabilities are sharply peaked, canonical equilibrium averages are equal to micro-canonical or isolated equilibrium averages. Accordingly, the remaining term is the unconstrained sub-system entropy,

$$\begin{aligned}
S_s(T) &= -k_B \langle \ln \hat{\rho}(T) \rangle_T \\
&= -k_B \text{Tr} \{ \hat{\rho}(T) \ln \hat{\rho}(T) \} \\
&= -k_B \int d\psi \frac{\langle \psi | \hat{\rho}(T) \ln \hat{\rho}(T) | \psi \rangle}{\langle \psi | \psi \rangle}.
\end{aligned} \tag{2.28}$$

This formula for the sub-system entropy is of the form, $S = -k_B \sum_{\alpha} \varphi_{\alpha} \ln \varphi_{\alpha}$, which is commonly called the information entropy. In the classical case it is variously attributed to Boltzmann, Gibbs, and Shannon, and it was popularized by Jaynes. In quantum mechanics it is called the von Neumann entropy, and it is written in terms of the density matrix, $S = -k_B \text{Tr} \rho \ln \rho$.²⁸⁻³⁰ It is commonly called ‘the’ entropy of the system, which implies that it is the entropy of the total system, when in fact it is only the sub-system part of the total entropy. Because most workers mistake this for the total entropy, it is commonly maximized to obtain equilibrium properties including the equilibrium probability distribution (e.g. Jaynes’ maxent approach to statistical mechanics). The consequences and problems with this common misinterpretation are detailed elsewhere.³²

One has to distinguish between the statistical mechanical and the thermodynamic definitions of the free

energy.¹ In statistical mechanics, the free energy corresponds to the unconstrained total entropy, whereas in thermodynamics the free energy corresponds to the maximal constrained total entropy. In the thermodynamic limit of an infinitely large sub-system and relatively negligible fluctuations, the two are equal. In statistical mechanics, in general the free energy is minus the temperature times the total entropy. For the present case of a sub-system exchanging energy with a thermal reservoir the statistical mechanical Helmholtz free energy is

$$\begin{aligned}
F_{\text{SM}}(T) &= -T S_{\text{tot}}(T) \\
&= -k_B T \ln Z(T) \\
&= \langle \hat{H} \rangle_T - T S_s(T).
\end{aligned} \tag{2.29}$$

This is the obvious analogue of the classical form for the Helmholtz free energy that one sees in standard thermodynamic texts. The main point to note is that it is the sub-system entropy that appears explicitly. All text books apart from the author’s^{1,2} call this term ‘the’ entropy, and imply that it is the entropy of the total system, which it clearly isn’t. The sub-system entropy that appears here is that of an unconstrained isolated system, Eq. (2.28). The second point to note that it is the average of the normalized energy that appears; this is extensive with the sub-system size, as is the sub-system entropy.

The thermodynamic free energy is minus the temperature times the maximum value of the constrained total entropy. By definition the most likely state maximizes the constrained total entropy. The most likely values of the energy and norm may be denoted by an overbar. In so far as the fluctuations are Gaussian, these are equal to the average values.

For the present canonical case, the thermodynamic Helmholtz free energy is

$$\begin{aligned}
F_{\text{TD}}(T) &= -T S_{\text{tot}}(\bar{E}|T) \\
&= \bar{E}(T) - T S_s(\bar{E}(T)).
\end{aligned} \tag{2.30}$$

The sub-system entropy that appears here is the constrained one given by the isolated system with specified values of energy. Note the difference between the most likely sub-system entropy, that appears here $S_s(\bar{E}(T))$, (this is approximately the unconstrained sub-system entropy, and is the sub-system entropy in the most likely sub-system energy macrostate), and the reservoir entropy in the most likely wave state that was used above, $\bar{S}_r \equiv S_r(\bar{\psi}) = S_0 = -E_0/T$. Note also that $S_s(\bar{E}(T)) \neq -\bar{E}(T)/T$, and that $\bar{E} \neq E(\bar{\psi}) \equiv E_0$.

There is an obvious identity between the functional forms for the thermodynamic and statistical mechanical Helmholtz free energies. The free energy is negative, assuming that the constant has been chosen to make the total entropy positive. The thermodynamic free energy is strictly greater (i.e. strictly smaller in magnitude) than the statistical mechanical free energy. In the thermodynamic limit of an infinitely large sub-system and relatively negligible fluctuations, the two are equal to a very good approximation.

III. TRANSITION PROBABILITY AND THE STOCHASTIC DISSIPATIVE SCHRÖDINGER EQUATION

The aim of this section is to derive the transition probability operator for a canonical equilibrium system, and from this to derive the stochastic dissipative Schrödinger equation. The strategy will follow closely the analogous derivation for the classical case.²

This section is primarily concerned with the wave state transition, $|\psi_1\rangle \xrightarrow{\tau} |\psi_2\rangle$. The time interval τ can be positive or negative and is initially of arbitrary duration; rather quickly a small τ expansion will be performed. One can consider the initial and final sub-system wave functions of the transition as belonging to distinct Hilbert spaces and form the direct product $H_1 \otimes H_2$, with the total wave function written as $|\psi_1\rangle |\psi_2\rangle \equiv |\psi_1, \psi_2\rangle$.

The analysis is based upon the second entropy operator, which may also be called the transition entropy operator, or the two-time entropy operator. For the transition in time τ , the unconditional transition probability operator is related to the second entropy operator by

$$\hat{\rho}^{(2)}(\tau) = \frac{e^{\hat{S}^{(2)}(\tau)/k_B}}{Z^{(2)}(\tau, T)}. \quad (3.1)$$

A detailed analysis of the second entropy in fluctuation approximation follows shortly. First, the time symmetries for an equilibrium system will be given explicitly.

A. Time Symmetry of the Adiabatic Propagator

There are two distinct time symmetries that result from Schrödinger's equation for a time-independent isolated quantum system, namely time reversibility and microscopic reversibility. In order to derive these one begins by noting that complex conjugation is the quantum operation that corresponds to the classical notion of velocity reversal. To see this, integrating Schrödinger's equation,

$$i\hbar|\dot{\psi}^0\rangle = \hat{H}|\psi\rangle, \quad (3.2)$$

gives the adiabatic time propagator as

$$\hat{U}^0(\tau) \equiv e^{\tau\hat{H}/i\hbar}. \quad (3.3)$$

By inspection one sees that there are two symmetries: The first symmetry is time reversibility,

$$\hat{U}^0(-\tau) = \hat{U}^0(\tau)^{-1}, \quad (3.4)$$

and, since the Hamiltonian is Hermitian, $\hat{H}^\dagger = \hat{H}$, and real $\hat{H}^* = \hat{H}$, the second symmetry is microscopic reversibility,

$$\hat{U}^0(\tau)^\dagger = \hat{U}^0(\tau)^* = \hat{U}^0(\tau)^{-1}. \quad (3.5)$$

Time reversibility says that the trajectory through any point is unique. Microscopic reversibility says that reversing the velocities reverses the transition, which is to

say that $\psi_1 \xrightarrow{\tau} \psi_2$ has reverse transition $\psi_2^* \xrightarrow{\tau} \psi_1^*$. In general, in consequence of microscopic reversibility the propagator is unitary. Note that time is *not* reversed in microscopic reversibility.

It should be emphasized that microscopic reversibility implies the dual symmetry $\hat{U}^0(\tau)^\dagger = \hat{U}^0(\tau)^{-1}$ and $\hat{U}^0(\tau)^* = \hat{U}^0(\tau)^{-1}$. By the definition that the Hermitian conjugate is the transpose of the complex conjugate, $\dagger \equiv *T$, these together imply the transpose symmetry of the propagator,

$$\hat{U}^0(\tau)^T = \hat{U}^0(\tau). \quad (3.6)$$

The reason why the double symmetry is implied by microscopic reversibility for a general equilibrium system is now discussed. Consider the evolution of the wave function,

$$|\psi_2\rangle = \hat{U}^0(\tau)|\psi_1\rangle. \quad (3.7)$$

The complex conjugate of a wave state is ψ^* , or $|\psi\rangle^* = |\psi^*\rangle$. Hence the evolution equation has complex conjugate

$$\begin{aligned} |\psi_2^*\rangle &= \hat{U}^0(\tau)^*|\psi_1^*\rangle = \hat{U}^0(\tau)^{-1}|\psi_1^*\rangle, \\ \text{or } |\psi_1^*\rangle &= \hat{U}^0(\tau)|\psi_2^*\rangle \end{aligned} \quad (3.8)$$

This says that if ψ_2 is the end result of the transition from ψ_1 in time τ , then ψ_1^* is the end result of the transition from ψ_2^* , also in time τ . This has the obvious meaning of reversing the transition, and that ψ^* is the same as the state ψ with all of the velocities reversed.

The complementary approach is to take the Hermitian conjugate of the same transition,

$$\begin{aligned} \langle\psi_2| &= \langle\psi_1|\hat{U}^0(\tau)^\dagger = \langle\psi_1|\hat{U}^0(\tau)^{-1}, \\ \text{or } \langle\psi_1| &= \langle\psi_2|\hat{U}^0(\tau). \end{aligned} \quad (3.9)$$

One can also see this as reversing the transition, with the interpretation that $\langle\psi|$ is the dual of the state $|\psi\rangle$ with all the velocities reversed.

For an open equilibrium quantum system, microscopic reversibility must still hold, because the stochastic, dissipative transitions of the sub-system are derived from adiabatic transitions of the total system.

B. Second Entropy Fluctuation Operator

1. Fluctuation Form

Recall that the fluctuation of the sub-system wave function is $\Delta\psi \equiv \psi - \bar{\psi}$. Assume that the second entropy for the transition has the quadratic fluctuation form

$$\begin{aligned} S^{(2)}(\psi_2, \psi_1; \tau) &= \langle\Delta\psi_2, \Delta\psi_1|\hat{\mathcal{A}}^{(2)}(\tau)|\Delta\psi_1, \Delta\psi_2\rangle + \bar{S}^{(1)} \\ &= \langle\Delta\psi_2|\hat{a}(\tau)|\Delta\psi_2\rangle + \langle\Delta\psi_1|\hat{c}(\tau)|\Delta\psi_1\rangle \\ &\quad + \langle\Delta\psi_2|\hat{b}(\tau)|\Delta\psi_1\rangle + \langle\Delta\psi_1|\hat{b}(\tau)^\dagger|\Delta\psi_2\rangle + \bar{S}^{(1)}. \end{aligned} \quad (3.10)$$

Note that the order of the arguments of the second entropy defines the time interval as the time of the first argument minus the time of the second argument, $S^{(2)}(\psi_2, \psi_1; \tau) \Rightarrow \tau \equiv t_2 - t_1$. The various operators are also a function of temperature, which is generally not shown. The final (immaterial) constant makes the maximum value of the second entropy equal to that of the first entropy $\bar{S}^{(1)}$ when the two termini are the most likely state, $\psi_1 = \psi_2 = \bar{\psi}$, which is related to the reduction condition discussed further below.^{2,33} The negative definite operator $\hat{A}^{(2)}(\tau)$ (equivalently its component operators $\hat{a}(\tau)$, $\hat{b}(\tau)$, and $\hat{c}(\tau)$) is the second entropy fluctuation operator, and, after its properties have been established, it will be used to give the second entropy operator itself, and hence the transition probability operator.

Three symmetries must hold: statistical symmetry,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1, \psi_2; -\tau), \quad (3.11)$$

reality,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_2, \psi_1; \tau)^*, \quad (3.12)$$

and microscopic reversibility,

$$S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1^*, \psi_2^*; \tau). \quad (3.13)$$

(Note that this means the conjugate of the fluctuation, $\Delta\psi^* \equiv \psi^* - \bar{\psi}^* = [\hat{I} - \hat{\mathcal{P}}_0]|\psi^*\rangle$.)

Statistical symmetry simply reflects the ordering of the arguments of the second entropy discussed above. It can also be called time homogeneity symmetry, since it follows by first shifting the time origin by t , $t_2 = t + \tau$ and $t_1 = t$, and then setting $t \Rightarrow -\tau$. The second entropy is real: because it is a physical observable (more precisely, a linear combination of physical observables with real coefficients), and also because its exponential gives the transition probability density, which is taken to be real. Microscopic reversibility is non-trivial and relies upon two facts: First, Schrödinger's equation for the total isolated system (sub-system plus reservoir) obeys microscopic reversibility. And second, for an equilibrium system, a wave state of the reservoir ψ_r and its conjugate ψ_r^* are equally probable, since conjugation represents velocity reversal.

Statistical symmetry implies that

$$\hat{a}(-\tau) = \hat{c}(\tau), \text{ and } \hat{b}(-\tau) = \hat{b}(\tau)^\dagger. \quad (3.14)$$

Reality implies that

$$\hat{a}(\tau)^\dagger = \hat{a}(\tau), \text{ and } \hat{c}(\tau)^\dagger = \hat{c}(\tau). \quad (3.15)$$

The form of the two cross terms in the second entropy guarantees reality for the contribution from these two terms. Microscopic reversibility implies that

$$\hat{a}(\tau)^* = \hat{c}(\tau), \text{ and } \hat{b}(\tau)^* = \hat{b}(\tau)^\dagger. \quad (3.16)$$

Hence $\hat{a}(\tau) = \hat{a}(\tau)^\dagger = \hat{a}(-\tau)^*$, and $\hat{b}(\tau) = \hat{b}(\tau)^* = \hat{b}(-\tau)^*$.

2. Most Likely Terminus

The derivative of the second entropy with respect to $\langle\psi_2|$ is

$$\frac{\partial S^{(2)}(\psi_2, \psi_1; \tau)}{\partial \langle\psi_2|} = \hat{a}(\tau) |\Delta\psi_2\rangle + \hat{b}(\tau) |\Delta\psi_1\rangle. \quad (3.17)$$

The most likely terminus of the transition, $\bar{\psi}_2 \equiv \bar{\psi}(\tau|\psi_1)$, follows by setting this derivative to zero,

$$|\Delta\bar{\psi}_2\rangle = -\hat{a}(\tau)^{-1}\hat{b}(\tau) |\Delta\psi_1\rangle. \quad (3.18)$$

3. Reduction Condition

The second entropy may be re-written in terms of the departure from the most likely terminus, $\Delta\psi_2 - \Delta\bar{\psi}_2 = \psi_2 - \bar{\psi}_2$,

$$\begin{aligned} S^{(2)}(\psi_2, \psi_1; \tau) = & \quad (3.19) \\ & \langle\psi_2 - \bar{\psi}_2 | \hat{a}(\tau) | \psi_2 - \bar{\psi}_2 \rangle \\ & + \langle\Delta\psi_1 | \left\{ \hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1} \hat{b}(\tau) \right\} | \Delta\psi_1 \rangle + \bar{S}^{(1)}. \end{aligned}$$

The reduction condition is that in the most likely state, the second entropy reduces to the first entropy,^{2,33}

$$\begin{aligned} S^{(2)}(\bar{\psi}_2, \psi_1; \tau) = & S^{(1)}(\psi_1|T) \\ = & \langle\Delta\psi_1 | \hat{S}'' | \Delta\psi_1 \rangle + \bar{S}^{(1)}. \quad (3.20) \end{aligned}$$

The reduction condition is equivalent to insisting that the transition probability must reduce to the probability of the initial state upon summing over all possible final states.^{2,33} This is the reason that it is the second derivative of the actual entropy and not the expectation entropy that is required for the fluctuation operator. The reduction condition therefore yields the requirement

$$\hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1} \hat{b}(\tau) = \hat{S}_r''. \quad (3.21)$$

This result must hold for each value of the time step τ .

4. Small Time Expansion

Since $\bar{\psi}_2 \rightarrow \psi_1$ as $\tau \rightarrow 0$, the second entropy must contain essentially a δ -function singularity. Hence the small- τ expansions must be of the form

$$\hat{a}(\tau) = \frac{1}{|\tau|} \hat{a}_{-1} + \frac{1}{\tau} \hat{a}'_{-1} + \hat{a}_0 + \hat{\tau} \hat{a}'_0 + \mathcal{O}(\tau), \quad (3.22)$$

$$\hat{b}(\tau) = \frac{1}{|\tau|} \hat{b}_{-1} + \frac{1}{\tau} \hat{b}'_{-1} + \hat{b}_0 + \hat{\tau} \hat{b}'_0 + \mathcal{O}(\tau), \quad (3.23)$$

and

$$\hat{c}(\tau) = \frac{1}{|\tau|} \hat{c}_{-1} + \frac{1}{\tau} \hat{c}'_{-1} + \hat{c}_0 + \hat{\tau} \hat{c}'_0 + \mathcal{O}(\tau), \quad (3.24)$$

with $\hat{\tau} \equiv \text{sign } \tau = \tau/|\tau|$.

The reason why the non-analytic terms appear (i.e. those containing $|\tau|$ and $\hat{\tau}$) is that these are necessary to yield the irreversible behavior that is characteristic of all thermodynamic evolution. One concludes that this is not a Taylor expansion for an infinitesimal time step, since this would only ever yield analytic terms, but rather an expansion for small but finite time steps that is a resummation of an infinite order Taylor expansion. The validity of beginning the expansion with terms $\mathcal{O}(\tau^{-1})$ can be judged by the consequences; amongst other things it yields a physically plausible stochastic Schrödinger equation with a conventional velocity for the wave function.

From the symmetries given above, $\hat{a}(\tau) = \hat{a}(\tau)^\dagger = \hat{a}(-\tau)^*$, and $\hat{a}(-\tau) = \hat{c}(\tau)$, one can see that the unprimed \hat{a} are real and self-adjoint and equal the unprimed \hat{c} , and the primed \hat{a} are imaginary and self-adjoint and equal the negative of the primed \hat{c} . Also, since $\hat{b}(\tau) = \hat{b}(\tau)^{* \dagger} = \hat{b}(-\tau)^*$, the unprimed \hat{b} are real and self-adjoint, and the primed \hat{b} are imaginary and anti-self-adjoint.

Since $\bar{\psi}_2 \rightarrow \psi_1$ as $\tau \rightarrow 0$, to leading order $\hat{a}(\tau) = -\hat{b}(\tau)$, which implies that

$$\hat{a}_{-1} = -\hat{b}_{-1} \equiv -\hat{\lambda}^{-1}, \text{ and } \hat{a}'_{-1} = -\hat{b}'_{-1} = \hat{0}. \quad (3.25)$$

From the symmetry relations, $\hat{\lambda}$ is a real Hermitian operator that is positive definite (because the second entropy must be negative definite). The primed coefficients individually vanish because \hat{a}'_{-1} is self-adjoint and \hat{b}'_{-1} is anti-self-adjoint. With these, the small time expansions read

$$\hat{a}(\tau) = \frac{-1}{|\tau|} \hat{\lambda}^{-1} + \hat{a}_0 + \hat{\tau} \hat{a}'_0 + \mathcal{O}(\tau), \quad (3.26)$$

$$\hat{b}(\tau) = \frac{1}{|\tau|} \hat{\lambda}^{-1} + \hat{b}_0 + \hat{\tau} \hat{b}'_0 + \mathcal{O}(\tau), \quad (3.27)$$

and

$$\hat{c}(\tau) = \frac{-1}{|\tau|} \hat{\lambda}^{-1} + \hat{a}_0 - \hat{\tau} \hat{a}'_0 + \mathcal{O}(\tau). \quad (3.28)$$

Inserting these expansions in the reduction condition, to zeroth order in the time step one must have

$$\begin{aligned} \hat{\hat{S}}_r'' &= \hat{c}(\tau) - \hat{b}(\tau)^\dagger \hat{a}(\tau)^{-1} \hat{b}(\tau) \\ &= \frac{-1}{|\tau|} \hat{\lambda}^{-1} + \hat{a}_0 - \hat{\tau} \hat{a}'_0 - \left[\frac{1}{|\tau|} \hat{\lambda}^{-1} + \hat{b}_0 - \hat{\tau} \hat{b}'_0 \right] \\ &\quad \times \left[\frac{-1}{|\tau|} \hat{\lambda}^{-1} + \hat{a}_0 + \hat{\tau} \hat{a}'_0 \right]^{-1} \left[\frac{1}{|\tau|} \hat{\lambda}^{-1} + \hat{b}_0 + \hat{\tau} \hat{b}'_0 \right] \\ &= \frac{-1}{|\tau|} \hat{\lambda}^{-1} + \hat{a}_0 - \hat{\tau} \hat{a}'_0 + \left[\frac{1}{|\tau|} \hat{\lambda}^{-1} + \hat{b}_0 - \hat{\tau} \hat{b}'_0 \right] \\ &\quad \times \left[\hat{\mathbb{I}} + |\tau| \hat{\lambda} \hat{a}_0 + \tau \hat{\lambda} \hat{a}'_0 \right] \left[\hat{\mathbb{I}} + |\tau| \hat{\lambda} \hat{b}_0 + \tau \hat{\lambda} \hat{b}'_0 \right] \\ &= \hat{a}_0 - \hat{\tau} \hat{a}'_0 + \hat{b}_0 - \hat{\tau} \hat{b}'_0 + \hat{a}_0 + \hat{\tau} \hat{a}'_0 + \hat{b}_0 + \hat{\tau} \hat{b}'_0 \\ &= 2 \left[\hat{a}_0 + \hat{b}_0 \right] + \mathcal{O}(\tau). \end{aligned} \quad (3.29)$$

In short,

$$\hat{a}_0 + \hat{b}_0 = \frac{1}{2} \hat{\hat{S}}_r'' = \frac{1}{2} \hat{\hat{S}}_r'. \quad (3.30)$$

This is formally the same as the result for classical fluctuations in macrostates or microstates given in Ref. 2.

5. Dissipative Schrödinger Equation

Using this, the expansion for the most likely terminal wave function departure becomes

$$\begin{aligned} |\Delta \bar{\psi}_2\rangle &= -\hat{a}(\tau)^{-1} \hat{b}(\tau) |\Delta \psi_1\rangle \\ &= \left[\hat{\mathbb{I}} + |\tau| \hat{\lambda} \hat{a}_0 + \tau \hat{\lambda} \hat{a}'_0 \right] \\ &\quad \times \left[\hat{\mathbb{I}} + |\tau| \hat{\lambda} \hat{b}_0 + \tau \hat{\lambda} \hat{b}'_0 \right] |\Delta \psi_1\rangle \\ &= |\Delta \psi_1\rangle + \tau \hat{\lambda} \left[\hat{a}'_0 + \hat{b}'_0 \right] |\Delta \psi_1\rangle \\ &\quad + \frac{|\tau|}{2} \hat{\lambda} \hat{\hat{S}}_r' |\Delta \psi_1\rangle + \mathcal{O}(\tau^2). \end{aligned} \quad (3.31)$$

Here the thermodynamic force operator has been used, $\hat{\hat{S}}_r' = \hat{\hat{S}}_r''$.

It is possible that variational procedures based upon the approximation $\hat{\hat{S}}_r' \approx \hat{S}_r'(\psi) + \mathcal{O}(\Delta\psi)$ might prove useful, although this does destroy the negative semi-definiteness of the entropy fluctuation operator (see below). In fact it is probably not too hard to estimate $\hat{\hat{S}}_r'$ since the required $S_0 \equiv S_r(\bar{\psi})$ can be taken to be the maximum value of $S_r(\psi)$ calculated thus far on the trajectory, and one can probably make the replacement $N(\bar{\psi}) \Rightarrow N(\psi)$, or else incorporate this constant into the dissipative operator.

The adiabatic evolution must be contained in the reversible term, which is the one that is proportional to τ , $|\psi_1^0\rangle = (1/i\hbar) \hat{\mathcal{H}} |\psi_1\rangle$. There may be reversible reservoir contributions, but since the reservoir is nothing but a perturbation to the adiabatic evolution, they can be neglected compared to the reversible adiabatic term. One cannot neglect the irreversible reservoir term because there is not adiabatic irreversible term with which to compare it. Since it is the only irreversible term, and since irreversibility is an essential ingredient in the evolution that follows directly from the second law of thermodynamics, one must retain the irreversible reservoir term.

Hence equating the reversible term here with the adiabatic evolution of the wave function, one must have

$$\hat{\lambda} \left[\hat{a}'_0 + \hat{b}'_0 \right] = \frac{1}{i\hbar} \hat{\mathcal{H}}. \quad (3.32)$$

With $|\Delta\psi\rangle \equiv |\psi\rangle - \hat{\mathcal{P}}_0 |\psi\rangle$, $\bar{\psi}_2 \equiv \bar{\psi}(t_2 | \psi_1, t_1)$, and using this result for the reversible evolution, the above expression for the evolution of the fluctuation may be rearranged to give the evolution of the wave function itself

with the ground state projection terms explicit,

$$\begin{aligned} |\bar{\psi}_2\rangle &= |\psi_1\rangle + \frac{\tau}{i\hbar} \hat{\mathcal{H}} |\psi_1\rangle + \frac{|\tau|}{2} \hat{\lambda} \hat{S}_r' |\psi_1\rangle \\ &\quad + \hat{\mathcal{P}}_0 |\bar{\psi}_2\rangle - \hat{\mathcal{P}}_0 |\psi_1\rangle - \frac{\tau}{i\hbar} \hat{\mathcal{H}} \hat{\mathcal{P}}_0 |\psi_1\rangle \\ &\quad - \frac{|\tau|}{2} \hat{\lambda} \hat{S}_r' \hat{\mathcal{P}}_0 |\psi_1\rangle + \mathcal{O}(\tau^2). \end{aligned} \quad (3.33)$$

Operating on both sides of this from the left with the ground state projector, and using the fact that the projector commutes with the Hamiltonian operator one obtains

$$0 = \frac{|\tau|}{2} \hat{\mathcal{P}}_0 \hat{\lambda} \hat{S}_r' |\psi_1\rangle - \frac{|\tau|}{2} \hat{\lambda} \hat{S}_r' \hat{\mathcal{P}}_0 |\psi_1\rangle. \quad (3.34)$$

Since $\hat{S}_r' \hat{\mathcal{P}}_0 |\psi_1\rangle = 0$, this proves that $\hat{\mathcal{P}}_0 \hat{\lambda} \hat{S}_r' = 0$. Hence in the entropy representation one must have $\lambda_{0n}^S = \lambda_{n0}^S = 0$, since $\hat{\lambda}$ is a symmetric operator. This says that the dissipative or drag operator does not couple the ground and excited states.

Using this, the projector terms cancel and the expression for the evolution of the full wave function is finally given by

$$\begin{aligned} |\bar{\psi}(t_2|\psi_1, t_1)\rangle &= |\psi_1\rangle + \frac{\tau}{i\hbar} \hat{\mathcal{H}} |\psi_1\rangle + \frac{|\tau|}{2} \hat{\lambda} \hat{S}_r' |\psi_1\rangle \\ &\quad + \mathcal{O}(\tau^2). \end{aligned} \quad (3.35)$$

This is the dissipative Schrödinger equation.

The final term in the dissipative Schrödinger equation is the gradient of the first entropy. This provides the thermodynamic driving force toward the most likely state. (Actually, this is only true if one has not evolved into the final equilibrium state. It is shown below that if the equilibrium probability operator is stationary, then the drag operator must commute with the entropy operator, and there is no mixing of entropy states due to this term.) It is the exact analogue of the dissipative term in the classical Langevin equation. In that case the dissipation is linearly proportional to the velocity, which itself is proportional to the velocity gradient of the entropy.

The operator $\hat{\lambda}$ may be called the dissipative operator, or statistical drag operator. From the symmetry requirements it must be Hermitian and real. Apart from this its magnitude can be chosen within wide bounds. In so far as the norm of the ground state projection $N(\bar{\psi})$ is a constant of the motion (see below), it can be taken out of the thermodynamic force operator and used effectively to rescale the dissipative operator. The thermodynamic force operator reflects the exchange with the thermal reservoir, and, as is always the case with the reservoir formalism, it is an abstraction of reality; the final results are not sensitive to its precise value (see next).

C. Stochastic, Dissipative Schrödinger Equation

1. Stochastic Contribution

Since the evolution of the sub-system wave function is determined in part by the interactions with the reservoir, and since the wave function of the reservoir is unknown, there must be a random element to the sub-system evolution, which is to say that it is only determined in a probabilistic sense, and it may not be the same each time that the sub-system visits the same sub-system wave state. Therefore, one must add a stochastic operator to the above deterministic equation to give the stochastic, dissipative Schrödinger equation,

$$\begin{aligned} |\psi_2\rangle &= |\psi_1\rangle + \frac{t_{21}}{i\hbar} \hat{\mathcal{H}} |\psi_1\rangle + \frac{|t_{21}|}{2} \hat{\lambda} \hat{S}_r' |\psi_1\rangle + \hat{\mathcal{R}} |\psi_1\rangle \\ &\equiv [\hat{\mathbf{I}} + \hat{u}(t_{21}) + \hat{\mathcal{R}}] |\psi_1\rangle \\ &\equiv \hat{\mathcal{U}}(t_{21}) |\psi_1\rangle. \end{aligned} \quad (3.36)$$

This is valid to linear order in the time step. Recall that the propagator is non-linear since the thermodynamic force is inversely proportional to the norm of the ground state projection, $N(\bar{\psi}_1)$. However, in so far as $N(\bar{\psi})$ is a constant of the motion (see below), it can be taken out of the thermodynamic force operator and used effectively to rescale the dissipative operator.

Note that for this open system and its stochastic dissipative Schrödinger equation, the time reversed propagator is not equal to the inverse, $\hat{\mathcal{U}}(t_1, t_2) \neq \hat{\mathcal{U}}(t_2, t_1)^{-1}$. This contrasts with an isolated system, where the explicit form for the adiabatic time propagator, $\hat{U}^0(t_2, t_1) \equiv \exp -i(t_2 - t_1)\hat{\mathcal{H}}/\hbar$, shows that $\hat{U}^0(t_1, t_2) = \hat{U}^0(t_2, t_1)^{-1}$. The difference between the two cases in the presence of the irreversible terms, those proportional to $|t_{21}|$, in the stochastic, dissipative Schrödinger equation.

2. Microscopic Reversibility

Let

$$|\psi_2\rangle = \hat{\mathcal{U}}(t_{21}) |\psi_1\rangle, \quad (3.37)$$

and

$$|\psi_4\rangle = \hat{\mathcal{U}}(t_{21}) |\psi_3\rangle. \quad (3.38)$$

These are stochastic equations. Choose $\psi_3 = \psi_2^*$. Then from microscopic reversibility one should have, on average, $\psi_4 = \psi_1^*$, or

$$\begin{aligned} |\psi_1^*\rangle &= \hat{\mathcal{U}}(t_{21}) |\psi_2^*\rangle \\ &= \hat{\mathcal{U}}(t_{21}) \hat{\mathcal{U}}(t_{21})^* |\psi_1^*\rangle. \end{aligned} \quad (3.39)$$

The second equality invokes the complex conjugate of the first expression. Since these are stochastic equations, this should hold on average, which leads to

$$\langle \hat{\mathcal{U}}(t_{21}) \hat{\mathcal{U}}(t_{21})^* \rangle_{\text{stoch}} = \hat{\mathbf{I}}. \quad (3.40)$$

3. Unitary Condition

This is in fact one form of the unitary condition, which ultimately comes from the reduction condition on the transition probability.³¹ The unitary condition can be written in eight equivalent forms using the fact that the identity operator is invariant under the operations of Hermitian conjugation, complex conjugation, and transposition,

$$\begin{aligned}\hat{\mathbf{I}} &= \left\langle \hat{\mathcal{U}}(t_{21}) \hat{\mathcal{U}}(t_{21})^\dagger \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{U}}(t_{21})^\dagger \hat{\mathcal{U}}(t_{21}) \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{U}}(t_{21})^T \hat{\mathcal{U}}(t_{21})^* \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{U}}(t_{21})^* \hat{\mathcal{U}}(t_{21})^T \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{U}}(t_{21})^* \hat{\mathcal{U}}(t_{21}) \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{U}}(t_{21}) \hat{\mathcal{U}}(t_{21})^* \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{U}}(t_{21})^\dagger \hat{\mathcal{U}}(t_{21})^T \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{U}}(t_{21})^T \hat{\mathcal{U}}(t_{21})^\dagger \right\rangle_{\text{stoch}}\end{aligned}\quad (3.41)$$

It can be seen that the fifth and sixth of these correspond to microscopic reversibility.

The unitary condition gives an expression for the variance of the stochastic operator. To linear order in the time step t_{21} , the first form of the unitary condition is

$$\begin{aligned}\hat{\mathbf{I}} &= \left\langle \left[\hat{\mathbf{I}} + \hat{\mathcal{U}}(t_{21}) + \hat{\mathcal{R}} \right] \left[\hat{\mathbf{I}} + \hat{\mathcal{U}}(t_{21}) + \hat{\mathcal{R}} \right]^\dagger \right\rangle_{\text{stoch}} \\ &= \hat{\mathbf{I}} + \hat{\mathcal{U}}(t_{21}) + \hat{\mathcal{U}}(t_{21})^\dagger + \left\langle \hat{\mathcal{R}} \hat{\mathcal{R}}^\dagger \right\rangle_{\text{stoch}} + \mathcal{O}(\tau^2) \quad (3.42) \\ &= \hat{\mathbf{I}} + \frac{|t_{21}|}{2} \left[\hat{\lambda} \hat{\mathcal{S}}_r' + \hat{\mathcal{S}}_r' \hat{\lambda}^\dagger \right] + \left\langle \hat{\mathcal{R}} \hat{\mathcal{R}}^\dagger \right\rangle_{\text{stoch}} + \mathcal{O}(t_{21}^2).\end{aligned}$$

The final equality follows after the stochastic average and neglecting terms higher than linear order in t_{21} . Note that $\hat{\lambda}$ and $\hat{\mathcal{S}}_r'$ are Hermitian; in fact they are real and transpose symmetric. This leads to eight expressions for the variance,

$$\begin{aligned}&\frac{-|t_{21}|}{2} \left[\hat{\lambda} \hat{\mathcal{S}}_r' + \hat{\mathcal{S}}_r' \hat{\lambda} \right] \\ &= \left\langle \hat{\mathcal{R}} \hat{\mathcal{R}}^\dagger \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{R}}^\dagger \hat{\mathcal{R}} \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{R}}^T \hat{\mathcal{R}}^* \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{R}}^* \hat{\mathcal{R}}^T \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{R}}^* \hat{\mathcal{R}} \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{R}} \hat{\mathcal{R}}^* \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{R}}^\dagger \hat{\mathcal{R}}^T \right\rangle_{\text{stoch}} = \left\langle \hat{\mathcal{R}}^T \hat{\mathcal{R}}^\dagger \right\rangle_{\text{stoch}}.\end{aligned}\quad (3.43)$$

The simplest way to make these eight expressions equivalent is to take the stochastic operator to be real and transpose symmetric, $\hat{\mathcal{R}} = \hat{\mathcal{R}}^T = \hat{\mathcal{R}}^*$. (One could argue that reality reflects the time symmetry of the reservoir.) In this case the unitary condition is simply

$$\left\langle \hat{\mathcal{R}}^2 \right\rangle_{\text{stoch}} = \frac{-|t_{21}|}{2} \left[\hat{\lambda} \hat{\mathcal{S}}_r' + \hat{\mathcal{S}}_r' \hat{\lambda} \right]. \quad (3.44)$$

Since $\hat{\mathcal{S}}_r'$ is negative semi-definite, and $\hat{\lambda}$ is positive semi-definite, one can see from this that the variance of the stochastic operator is Hermitian, positive semi-definite, and proportional to the length of the time step. As

is argued below, this is the fundamental form of the fluctuation-dissipation theorem.

Taking the stochastic operator to be to be real and transpose symmetric means that it is Hermitian $\hat{\mathcal{R}}^\dagger = \hat{\mathcal{R}}$. As just mentioned it depends upon the absolute value of the times step. It will be shown below that in the case that the probability operator is stationary, the dissipative operator and the thermodynamic force operator commute $\hat{\lambda} \hat{\mathcal{S}}_r' = \hat{\mathcal{S}}_r' \hat{\lambda}$. Both are also Hermitian operators. In this case, from the explicit expression for the stochastic dissipative time propagator, Eq. (3.36), one sees therefore that the time propagator has the symmetry

$$\hat{\mathcal{U}}(t_{21})^\dagger = \hat{\mathcal{U}}(t_{12}). \quad (3.45)$$

This is equivalent to the symmetry identified for the classical conditional transition probability density in Eq. (7.164) of Ref. 2, $\wp(\mathbf{\Gamma}_2 | \mathbf{\Gamma}_1, \Delta_t) = \wp(\mathbf{\Gamma}_2^\dagger | \mathbf{\Gamma}_1^\dagger, -\Delta_t)$.

4. Stationarity Condition

The time evolution of the probability operator is³¹

$$\begin{aligned}\hat{\wp}(t) &= \left\langle \hat{\mathcal{U}}(t) \hat{\wp}(0) \hat{\mathcal{U}}(t)^\dagger \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{U}}(t)^\dagger \hat{\wp}(0) \hat{\mathcal{U}}(t) \right\rangle_{\text{stoch}}.\end{aligned}\quad (3.46)$$

In so far as the probability operator equals the density operator, this is like a stochastic form of the conventional Lindblad master equation in the Krauss representation. It should be noted that the present formula, in addition to being stochastic, has been derived with explicit terms that abstract from a specific model for the reservoir, and that it obeys the exact unitary and irreversibility symmetry rules that are derived from the underlying Schrödinger equation for the total isolated system and the equilibrium nature of the reservoir.

Under the equilibrium stochastic, dissipative equations of motion, the Maxwell-Boltzmann probability operator should be stationary,

$$\begin{aligned}\hat{\wp}_{\text{MB}} &= \left\langle \hat{\mathcal{U}}(t) \hat{\wp}_{\text{MB}} \hat{\mathcal{U}}(t)^\dagger \right\rangle_{\text{stoch}} \\ &= \left\langle \hat{\mathcal{U}}(t)^\dagger \hat{\wp}_{\text{MB}} \hat{\mathcal{U}}(t) \right\rangle_{\text{stoch}},\end{aligned}\quad (3.47)$$

where $\hat{\wp}_{\text{MB}} = Z(T)^{-1} e^{\hat{\mathcal{S}}_r/k_B} = Z(T)^{-1} e^{-\hat{\mathcal{H}}/k_B T}$.

The stationarity condition is a very strong condition to impose. It will be shown below that it implies that there is no mixing between entropy modes: not only is the Maxwell-Boltzmann probability operator stationary, but any probability operator that corresponds to the density matrix constructed from the initial wave function is constant on the trajectory; even a non-equilibrium distribution of entropy modes is conserved. In a literal sense this is consistent with the present theory being purely an equilibrium theory: neither the equilibrium nor any other

distribution of entropy states evolves. The theory, however, would be somewhat more useful in a practical sense if the stochastic, dissipative propagator evolved an initial non-equilibrium distribution over time into the equilibrium distribution, so that the density matrix constructed from the wave function on the trajectory converged to the equilibrium probability operator. This can only be done if the propagator is constructed to violate the stationarity condition. For the present the consequences of imposing the stationarity condition will be pursued, and further discussion of the issue is deferred.

To linear order in the time step, the two forms of the stationarity condition yield

$$\frac{-|t_{21}|}{2} \left[e^{\hat{S}_r/k_B} \hat{\lambda} \hat{\bar{S}}_r' + \hat{\bar{S}}_r' \hat{\lambda} e^{\hat{S}_r/k_B} \right] = \left\langle \hat{\mathcal{R}} e^{\hat{S}_r/k_B} \hat{\mathcal{R}}^\dagger \right\rangle_{\text{stoch}}, \quad (3.48)$$

and

$$\frac{-|t_{21}|}{2} \left[e^{\hat{S}_r/k_B} \hat{\bar{S}}_r' \hat{\lambda} + \hat{\lambda} \hat{\bar{S}}_r' e^{\hat{S}_r/k_B} \right] = \left\langle \hat{\mathcal{R}}^\dagger e^{\hat{S}_r/k_B} \hat{\mathcal{R}} \right\rangle_{\text{stoch}}. \quad (3.49)$$

The adiabatic evolution has canceled here because the Hamiltonian operator commutes with the probability operator. Since the stochastic operator is taken to be real and symmetric, the two right hand sides are equal.

If $\hat{\mathcal{R}}$ and \hat{S}_r (equivalently $\hat{\phi}$) commute, then this is automatically satisfied if the unitary condition is satisfied. This will occur if $\hat{\mathcal{R}}$ is constructed from entropy eigenfunctions, which is indeed the case as is discussed below.

5. Entropy Representation in the Stationary Case

One can obtain the explicit form of the dissipative and stochastic operators by invoking the entropy representation in the stationary case. For the reasons discussed below, in practical terms the stationary condition is too restrictive. For computational approaches to equilibrium systems one should only impose the unitary condition, in which case most of the results given in this section do not hold.

In order to simplify the notation, the entropy eigenfunctions will be written with a single Roman letter, $\hat{S}_r |\zeta_n^S\rangle = S_n |\zeta_n^S\rangle$. A more precise notation would single out the principle and degenerate entropy states, $\hat{S}_r |\zeta_{\alpha g}^S\rangle = S_\alpha |\zeta_{\alpha g}^S\rangle$. The sums that follow are over all entropy states; references to the vanishing of correlations between states, or to only intra-state terms surviving should be taken to mean principle entropy states only.

The entropy eigenfunctions are also eigenfunctions of the thermodynamic force operator, $\hat{\bar{S}}_r' |\zeta_n^S\rangle = \bar{S}_n' |\zeta_n^S\rangle$, with the eigenvalue being

$$\bar{S}_n' \equiv \frac{k_B}{N(\psi)} \left[\frac{e^{S_n/k_B}}{e^{S_0/k_B}} - 1 \right]. \quad (3.50)$$

These are obviously negative (or zero for the ground state), and the depend upon the projection of wave function onto the ground state.

In the entropy representation the unitary condition, Eq. (3.44), is

$$\sum_l \langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} = \frac{-|t_{21}|}{2} [\lambda_{mn}^S \bar{S}_n' + \bar{S}_m' \lambda_{mn}^S]. \quad (3.51)$$

Recall that $\hat{\mathcal{R}}$ has been taken to be a real, symmetric operator. One stationarity condition is

$$\begin{aligned} \sum_l e^{S_l/k_B} \langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} \\ = \frac{-|t_{21}|}{2} \left[e^{S_m/k_B} \lambda_{mn}^S \bar{S}_n' + \bar{S}_m' \lambda_{mn}^S e^{S_n/k_B} \right] \end{aligned} \quad (3.52)$$

and the other is

$$\begin{aligned} \sum_l e^{S_l/k_B} \langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} \\ = \frac{-|t_{21}|}{2} \left[e^{S_m/k_B} \bar{S}_m' \lambda_{mn}^S + \lambda_{mn}^S \bar{S}_n' e^{S_n/k_B} \right] \end{aligned} \quad (3.53)$$

Subtracting these last two, one obtains

$$\begin{aligned} 0 &= e^{S_m/k_B} \lambda_{mn}^S \bar{S}_n' + \bar{S}_m' \lambda_{mn}^S e^{S_n/k_B} \\ &\quad - e^{S_m/k_B} \bar{S}_m' \lambda_{mn}^S - \lambda_{mn}^S \bar{S}_n' e^{S_n/k_B} \\ &= e^{S_m/k_B} \lambda_{mn}^S [\bar{S}_n' - \bar{S}_m'] \\ &\quad + \lambda_{mn}^S e^{S_n/k_B} [\bar{S}_m' - \bar{S}_n'] \\ &= -\lambda_{mn}^S [\bar{S}_m' - \bar{S}_n'] [e^{S_m/k_B} - e^{S_n/k_B}]. \end{aligned} \quad (3.54)$$

Since $S_m > S_n$ if $m > n$ (more precisely, $S_{\alpha g} > S_{\gamma h}$ if $\alpha > \gamma$), this implies

$$\lambda_{mn}^S = \lambda_{nn}^S \delta_{mn}. \quad (3.55)$$

Hence the drag or dissipative operator must be diagonal in the entropy representation and so it must be constructed from the entropy eigenfunctions,

$$\hat{\lambda} \equiv \sum_n \lambda_n |\zeta_n^S\rangle \langle \zeta_n^S|. \quad (3.56)$$

(The diagonalization holds for the principle entropy states only; the most general dissipative operator is of the form $\hat{\lambda} \equiv \sum_{\alpha, gh} \lambda_{\alpha, gh} |\zeta_{\alpha g}^S\rangle \langle \zeta_{\alpha h}^S|$.) This gives $\hat{\lambda} |\zeta_n^S\rangle = \lambda_n |\zeta_n^S\rangle$. Because $\hat{\lambda}$ is a real Hermitian operator, the λ_n must be real. It may be called the drag coefficient for the state ζ_n^S . One can set $\lambda_0 = 0$ since it always multiplies the thermodynamic force, which vanishes in the ground state, $\bar{S}_0' = 0$. (This results holds even when the stationarity condition doesn't.) Obviously, this construction means that the drag operator commutes with the entropy operator, the thermodynamic force operator, the probability operator, and the Hamiltonian operator. One sees from this that there can be no dissipative coupling between principle entropy states. There can be dissipative coupling between degenerate entropy states.

It should be noted that the dissipative operator is only diagonal if the stationarity condition holds. If one does

not insist upon the stationarity condition, then there can be dissipative coupling between the principle entropy states. In this case the variance of the stochastic operator is determined by the unitary condition alone, Eq. (3.51). In this case one expects that the thermodynamic force will tend to drive the wave function toward high entropy states, and that in combination with the stochastic force it will cause the density matrix to converge on the equilibrium probability operator.

With this diagonal form for the dissipative operator the stationarity condition becomes

$$\sum_l \langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} = -|t_{21}| \lambda_{mm}^S \bar{S}_m' \delta_{mn}, \quad (3.57)$$

and either unitary condition is

$$\sum_l e^{S_l/k_B} \langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} = -|t_{21}| e^{S_m/k_B} \lambda_{mm}^S \bar{S}_m' \delta_{mn}. \quad (3.58)$$

If one sets $n = m = 0$, both right hand sides vanish, since $\bar{S}_m' = 0$. Since both left hand sides are sums of non-negative terms, one sees that one must have

$$\langle R_{0l}^S R_{l0}^S \rangle_{\text{stoch}} = 0, \quad l = 0, 1, \dots \quad (3.59)$$

This means there is no stochastic coupling between the ground state and the excited states. It was already shown that there is no dissipative coupling in the ground state. There is no adiabatic coupling between the ground state and the excited states (because the Hamiltonian operator commutes with the entropy operator it is diagonal in the entropy representation). These mean that in general the ground state evolves independently of the excited states.

A sufficient condition that makes the left hand sides of the unitary and stationarity conditions proportional to a Kronecker-delta function is that the stochastic operators between different pairs of modes are uncorrelated,

$$\langle R_{ml}^S R_{ln}^S \rangle_{\text{stoch}} \equiv \langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} \delta_{mn}. \quad (3.60)$$

The conditions now become

$$\sum_{l>0} \langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} = -|t_{21}| \lambda_{mm}^S \bar{S}_m', \quad (3.61)$$

and

$$\sum_{l>0} e^{S_l/k_B} \langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} = -|t_{21}| e^{S_m/k_B} \lambda_{mm}^S \bar{S}_m'. \quad (3.62)$$

If one multiplies both sides of the first by e^{S_m/k_B} , and subtracts these two, then one obtains

$$\sum_{l>0} [e^{S_m/k_B} - e^{S_l/k_B}] \langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} = 0. \quad (3.63)$$

Setting $m = 1$, one sees that both factors in the summand are non-negative, since $S_m > S_n$ if $m > n$. Hence

one concludes that there is no stochastic coupling between the first excited state and the more excited states, $\langle R_{1l}^S R_{l1}^S \rangle_{\text{stoch}} = 0$ if $l > 1$. The equation now becomes

$$\sum_{l>1} [e^{S_m/k_B} - e^{S_l/k_B}] \langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} = 0. \quad (3.64)$$

Setting $m = 2$, one sees that there is no stochastic coupling to the second excited state from the even more excited states. Continuing in this fashion, one concludes that each principle entropy state is only coupled stochastically to itself,

$$\langle R_{ml}^S R_{lm}^S \rangle_{\text{stoch}} = \langle R_{mm}^S R_{mm}^S \rangle_{\text{stoch}} \delta_{ml}. \quad (3.65)$$

It follows that the stochastic operator, like the dissipative operator, is diagonal in the entropy representation,

$$\hat{\mathcal{R}} \equiv \sum_n r_n |\zeta_n^S\rangle \langle \zeta_n^S|. \quad (3.66)$$

(Again, the diagonalization holds for the principle entropy states only; the most general stochastic operator is of the form $\hat{\mathcal{R}} \equiv \sum_{\alpha,gh} r_{\alpha,gh} |\zeta_{\alpha g}^S\rangle \langle \zeta_{\alpha h}^S|$. Here the r_n are random real numbers of zero mean. With this $\hat{\mathcal{R}}|\zeta_n^S\rangle = r_n |\zeta_n^S\rangle$, and the stochastic operator commutes with the entropy operator. This means that the unitary condition automatically implies the stationarity condition, and that the variance of the coefficients is given by

$$\langle r_n^2 \rangle_{\text{stoch}} = -|t_{21}| \bar{S}_n' \lambda_n. \quad (3.67)$$

Note that the right hand side is inversely proportional to the magnitude of the projection of the current wave function onto the ground state. (Actually, because there is no mixing with the ground state, the norm of the ground state projection is a constant of the motion that can be taken out of the thermodynamic force operator and incorporated into a renormalized dissipative force operator.) This is a form of the quantum fluctuation-dissipation theorem. Since the thermodynamic force eigenfunctions are negative or zero, and since the drag operator coefficients are positive or zero, one can see that the variance of the random coefficients is positive or zero.

As was the case with the dissipative operator, the stochastic operator is only diagonal if the stationarity condition holds. If one does not insist upon the stationarity condition, then there can be stochastic coupling between the principle entropy states, Eq. (3.51). In this case one expects that combination of the thermodynamic force and the stochastic force it will cause the density matrix to converge to the equilibrium probability operator.

The simplest implementation of the above is to use a single dissipative coefficient and a single stochastic coefficient. Both operators can be made proportional to the thermodynamic force operator,

$$\hat{\lambda} = -\lambda \hat{S}'(\bar{\psi}), \quad \text{and} \quad \hat{R} = r \hat{S}'(\bar{\psi}), \quad (3.68)$$

with λ real and positive. In this case also the unitary condition and the stationary condition yield the same variance, namely

$$\langle r^2 \rangle_{\text{stoch}} = |\tau| \lambda. \quad (3.69)$$

Equation (3.67) and Eq. (3.69) are forms of the quantum fluctuation dissipation theorem. They say that the variance of the stochastic operator, which controls the fluctuation, must be linearly proportional to the drag operator, which controls the dissipation. The variance is proportional to the duration of the time step, so it is an irreversible contribution to the evolution of the wave function.

The stationarity condition is an optional condition that should only be imposed if the initial wave function obeys the equilibrium distribution. It is only if this condition is imposed that the dissipative and stochastic operators are diagonal in the entropy basis and that the entropy modes do not mix. In practical terms it is better *not* to impose the stationarity condition as this allows an arbitrary starting wave function. One should impose the unitary condition, with the dissipative operator and the stochastic operator *not* being diagonal in the entropy basis. In this way the trajectory of an arbitrary starting wave function will yield a density matrix that converges to the equilibrium probability operator and fluctuate about it, with the superposition states averaging to zero over the trajectory. A time average of the expectation value of an operator will then equal the equilibrium statistical average. The unitary condition must be imposed, and when it is the only such condition on the propagator the operators are not diagonal and do not need to be represented in the entropy basis. For this reason one can arguably regard the unitary condition as *the* quantum fluctuation dissipation theorem.

D. Transition Probability Operator and Time Correlation Function

1. Time Correlation Function

The transition probability operator is just the exponential of the second entropy operator,

$$\hat{\phi}^{(2)}(\tau, T) = \frac{1}{Z^{(2)}(\tau, T)} e^{\hat{S}^{(2)}(\tau, T)/k_B}. \quad (3.70)$$

With it, the statistical average of a two-time operator $\hat{O}^{(2)}$ is

$$\begin{aligned} \langle \hat{O}^{(2)} \rangle_{\tau, T} &= \int d\psi_1 d\psi_2 \frac{\langle \psi_2, \psi_1 | \hat{\phi}^{(2)} \hat{O}^{(2)} | \psi_1, \psi_2 \rangle}{\langle \psi_2, \psi_1 | \psi_1, \psi_2 \rangle} \\ &= \frac{1}{Z^{(2)}} \int d\psi_1 d\psi_2 \frac{1}{N(\psi_1)N(\psi_2)} \\ &\quad \times \sum_{\substack{m_2, n_2 \\ m_1, n_1}} \psi_{2, m_2}^* \psi_{2, n_2} \psi_{1, m_1}^* \psi_{1, n_1} \end{aligned}$$

$$\begin{aligned} &\times \left\{ e^{\hat{S}^{(2)}(\tau, T)/k_B} \hat{O}^{(2)} \right\}_{\substack{m_2, n_2 \\ m_1, n_1}} \\ &= \frac{\text{const.}}{Z^{(2)}} \sum_{m_2, m_1} \left\{ e^{\hat{S}^{(2)}(\tau, T)/k_B} \hat{O}^{(2)} \right\}_{\substack{m_2, m_2 \\ m_1, m_1}} \\ &= \text{Tr}^{(2)} \left\{ \hat{\phi}^{(2)}(\tau, T) \hat{O}^{(2)} \right\}. \end{aligned} \quad (3.71)$$

In passing to the third equality, the same trick as in Eq. (2.3) has been used, namely that all the terms in the integrand are odd except those with $m_2 = n_2$ and $m_1 = n_1$. This is the dual collapse of the wave functions at the termini of the transition. Once the representation of the product of the operators has been taken outside of the integral, what remains is the same for all indices, and hence the integral is a constant that can be taken outside of the sum and incorporated into the partition function.

The transition probability operator is $\hat{\phi}^{(2)}(\tau, T) \equiv e^{\hat{S}^{(2)}(\tau, T)/k_B} / Z'^{(2)}$ with the partition function being

$$\begin{aligned} Z'^{(2)}(\tau, T) &= \text{Tr}^{(2)} e^{\hat{S}^{(2)}(\tau, T)/k_B} \\ &= \sum_{m_2, m_1} \langle \zeta_{m_2}, \zeta_{m_1} | e^{\hat{S}^{(2)}(\tau, T)/k_B} | \zeta_{m_1}, \zeta_{m_2} \rangle, \end{aligned} \quad (3.72)$$

with the ζ being an arbitrary orthonormal basis. The elements of the transition matrix are explicitly

$$\wp_{\substack{m_2, n_2 \\ m_1, n_1}}^{(2)} = \langle \zeta_{m_2}, \zeta_{m_1} | \hat{\phi}^{(2)}(\tau, T) | \zeta_{n_1}, \zeta_{n_2} \rangle, \quad (3.73)$$

and similarly for the operator matrix. Hence the two-time trace is explicitly

$$\text{Tr}^{(2)} \left\{ \hat{\phi}^{(2)} \hat{O}^{(2)} \right\} = \sum_{\substack{m_2, n_2 \\ m_1, n_1}} \wp_{\substack{m_2, n_2 \\ m_1, n_1}}^{(2)} O_{\substack{n_2, m_2 \\ n_1, m_1}}^{(2)}. \quad (3.74)$$

A common quantity is the time correlation of two one-time operators. To obtain this one can introduce the diagonal two-time operator, $\hat{D}_{BA}^{(2)}$, which has the expectation

$$\frac{\langle \psi_2, \psi_1 | \hat{D}_{BA}^{(2)} | \psi_1, \psi_2 \rangle}{N(\psi_1)N(\psi_2)} = \frac{\langle \psi_2 | \hat{B} | \psi_2 \rangle}{N(\psi_2)} \frac{\langle \psi_1 | \hat{A} | \psi_1 \rangle}{N(\psi_1)}. \quad (3.75)$$

The time correlation function will shortly be expressed in terms of this and the transition probability operator.

Choose $\langle \hat{A} \rangle_{\text{stat}} = \langle \hat{B} \rangle_{\text{stat}} = 0$. Define the time correlation function as

$$C_{BA}(\tau) = \left\langle \hat{B}(\tau) \hat{A}(0) \right\rangle_{\text{stat}} = \left\langle \hat{A}(0) \hat{B}(\tau) \right\rangle_{\text{stat}}. \quad (3.76)$$

For a two-time average such as this, the positional order of the operators is irrelevant because the sign of τ gives the order of their application. This contrasts with a one-time average, where it is conventional that the position of the operators in the equation designates the time order of their application, which is to say that they are applied in order from right to left. The order of course is significant if the operators don't commute.

In view of the definitions of the two-time and one-time averages, in the zero time limit one has

$$C_{BA}(0^+) = \langle \hat{B}\hat{A} \rangle_{\text{stat}} \quad \text{and} \quad C_{BA}(0^-) = \langle \hat{A}\hat{B} \rangle_{\text{stat}}. \quad (3.77)$$

The right hand sides are one-time averages, which are here signified by the absence of a time argument. These expressions mean that if the operators don't commute, then there is a discontinuity at $\tau = 0$.

Time homogeneity means that the time correlation function must be invariant to a shift in the time origin. Hence first changing $\tau \Rightarrow t + \tau$, and then setting $t = -\tau$, such that $\hat{B}(\tau)\hat{A}(0) \Rightarrow \hat{B}(t+\tau)\hat{A}(t) \Rightarrow \hat{B}(0)\hat{A}(-\tau)$, must leave the time correlation function unchanged. From this one concludes that

$$C_{AB}(\tau) = C_{BA}(-\tau). \quad (3.78)$$

This can be called time homogeneity or statistical symmetry.

In view of the above, the small time expansion of the time correlation function must be of the form

$$C_{AB}(\tau) = C_{AB;0} + \hat{\tau}C'_{AB;0} + |\tau|C_{AB;1} + \tau C'_{AB;1}, \quad (3.79)$$

with

$$C_{AB;0} = \frac{1}{2} \langle \hat{A}\hat{B} + \hat{B}\hat{A} \rangle_{\text{stat}}, \quad (3.80)$$

and

$$C'_{AB;0} = \frac{1}{2} \langle \hat{A}\hat{B} - \hat{B}\hat{A} \rangle_{\text{stat}}. \quad (3.81)$$

In terms of the diagonal two-time operator and the transition probability operator, and not explicitly showing the temperature dependence, the time correlation function is

$$\begin{aligned} C_{BA}(\tau) &\equiv \langle \hat{D}_{BA}^{(2)} \rangle_{\text{stat}} \\ &= \text{Tr}^{(2)} \left\{ \hat{\wp}^{(2)}(\tau) \hat{D}_{BA}^{(2)} \right\} \\ &= \sum_{\substack{m_2, n_2 \\ m_1, n_1}} \wp_{m_2, n_2}^{(2)}(\tau) B_{n_2, m_2} A_{n_1, m_1}. \end{aligned} \quad (3.82)$$

If one uses the basis $\{\zeta_n^A\}$ for ψ_1 and $\{\zeta_n^B\}$ for ψ_2 , then the operator matrices are diagonal and this becomes

$$\begin{aligned} C_{BA}(\tau) &= \sum_{\substack{n_2 \\ n_1}} \wp_{n_2, n_1}^{(2), BA}(\tau) B_{n_2, n_2}^B A_{n_1, n_1}^A \\ &\equiv \sum_{n_2, n_1} \wp_{n_2, n_1}^{(2), BA}(\tau) B_{n_2, n_2}^B A_{n_1, n_1}^A. \end{aligned} \quad (3.83)$$

One can therefore identify $\wp_{mn}^{(2), BA}(\tau)$ as the unconditional probability of the transition between states of the two operators, $n^A \xrightarrow{\tau} m^B$. Explicitly this is

$$\wp_{mn}^{(2), BA}(\tau) \equiv \wp_{m, m}^{(2), BA}(\tau) = \langle \zeta_m^B, \zeta_n^A | \hat{\wp}^{(2)}(\tau) | \zeta_n^A, \zeta_m^B \rangle. \quad (3.84)$$

In view of the time homogeneity (statistical) symmetry, Eq. (3.78), the above representation of the time correlation function, Eq. (3.82), shows that

$$\wp_{m_2, n_2}^{(2)}(\tau) = \wp_{m_1, n_1}^{(2)}(-\tau). \quad (3.85)$$

One can see explicitly that this condition is guaranteed by the statistical symmetry of the second entropy, Eq. (3.11), $S^{(2)}(\psi_2, \psi_1; \tau) = S^{(2)}(\psi_1, \psi_2; -\tau)$, or, equivalently, $\hat{a}(-\tau) = \hat{c}(\tau)$ and $\hat{b}(-\tau) = \hat{b}(\tau)^\dagger$.

2. Time Correlation with Propagator

It is desired to write the time correlation function as a one time trace involving the stochastic time propagator. The most straightforward expression is

$$\begin{aligned} C_{BA}(\tau) &= \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{A} \hat{\wp} \rangle_{\text{stoch}} \\ &= \text{Tr}^{(1)} \langle \hat{U}(-\tau)^\dagger \hat{A} \hat{U}(-\tau) \hat{B} \hat{\wp} \rangle_{\text{stoch}}. \end{aligned} \quad (3.86)$$

For non-zero $\tau > 0$, both forms unambiguously signify that the operator \hat{A} is applied before the operator \hat{B} , and *vice versa* for $\tau < 0$. Unfortunately, due to the discontinuity in the time correlation function, there is an ambiguity in this expression at $\tau = 0$.

To circumvent this problem, and because of the convention that the operators are applied in order from right to left for one-time averages, one needs to define the operator

$$\begin{aligned} \hat{\eta}_{BA}(\tau) &= \frac{1 + \hat{\tau}}{2} \hat{B} + \frac{1 - \hat{\tau}}{2} \hat{A} \\ &= \begin{cases} \hat{B}, & \tau > 0, \\ \hat{A}, & \tau < 0. \end{cases} \end{aligned} \quad (3.87)$$

Recall that $\hat{\tau} \equiv \text{sign } \tau$. With this the time correlation function in singlet form is

$$C_{BA}(\tau) = \text{Tr}^{(1)} \langle \hat{U}(|\tau|)^\dagger \hat{\eta}_{BA}(\tau) \hat{U}(|\tau|) \hat{\eta}_{BA}(-\tau) \hat{\wp} \rangle_{\text{stoch}}. \quad (3.88)$$

The definitions have the effect that the operator that is applied first in time always occupies the right hand position, which is the usual convention for non-commuting operators. In addition, the time propagator always proceeds in the positive time direction. Since $\hat{\eta}_{AB}(-\tau) = \hat{\eta}_{BA}(\tau)$, it is clear that $C_{BA}(-\tau) = C_{AB}(\tau)$, as required.

Explicitly the time correlation function is

$$\begin{aligned} C_{BA}(\tau) &= \begin{cases} \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{A} \hat{\wp} \rangle_{\text{stoch}}, & \tau > 0, \\ \text{Tr}^{(1)} \langle \hat{U}(-\tau)^\dagger \hat{A} \hat{U}(-\tau) \hat{B} \hat{\wp} \rangle_{\text{stoch}}, & \tau < 0 \end{cases} \\ &= \begin{cases} \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{A} \hat{\wp} \rangle_{\text{stoch}}, & \tau > 0, \\ \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{\wp} \hat{A} \rangle_{\text{stoch}}, & \tau < 0. \end{cases} \end{aligned} \quad (3.89)$$

The second equality uses the facts that the trace is invariant to cyclic permutations of the operators, that $\hat{U}(-\tau) = \hat{U}(\tau)^\dagger$, and that the equilibrium probability operator and the time propagator commute. In the limit $\tau \rightarrow 0$, $\hat{U}(\tau) \rightarrow \hat{I}$, and

$$C_{BA}(0^+) = \text{Tr}^{(1)} \hat{B} \hat{A} \hat{\rho} = \langle \hat{B} \hat{A} \rangle_{\text{stat}} \quad (3.90)$$

and

$$C_{BA}(0^-) = \text{Tr}^{(1)} \hat{A} \hat{B} \hat{\rho} = \langle \hat{A} \hat{B} \rangle_{\text{stat}}, \quad (3.91)$$

as required.

In a particular representation of the operators, the average that is the time correlation function for $\tau > 0$ is

$$\begin{aligned} C_{BA}(\tau) &= \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{A} \hat{\rho} \rangle_{\text{stoch}}, \quad \tau > 0 \\ &= \sum_{\substack{m_2, n_2 \\ m_1, n_1}} \sum_l \langle \mathcal{U}_{m_1, n_2}(\tau)^\dagger \mathcal{U}_{m_2, l}(\tau) \wp_{n_1, m_1} \rangle_{\text{stoch}} \\ &\quad \times B_{n_2, m_2} A_{l, n_1} \\ &= \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{\rho} \hat{B} \hat{U}(\tau) \hat{A} \rangle_{\text{stoch}} \\ &= \sum_{\substack{m_2, n_2 \\ m_1, n_1}} \sum_l \langle \mathcal{U}_{m_1, l}(\tau)^\dagger \mathcal{U}_{n_2, n_1}(\tau) \wp_{l, m_2} \rangle_{\text{stoch}} \\ &\quad \times B_{m_2, n_2} A_{n_1, m_1}. \end{aligned} \quad (3.92)$$

The third equality uses the fact that the time propagator and the probability operator commute. Comparing this to the third equality in Eq. (3.88), this implies that the representation of the transition probability operator in terms of time propagators is

$$\begin{aligned} \wp_{m_2, n_2}^{(2)}(\tau) & \quad (3.93) \\ &= \sum_l \langle \mathcal{U}_{l, n_2}(\tau)^\dagger \mathcal{U}_{m_2, n_1}(\tau) \wp_{m_1, l} \rangle_{\text{stoch}}, \quad \tau > 0 \\ &= \sum_l \langle \mathcal{U}_{m_1, l}(\tau)^\dagger \mathcal{U}_{m_2, n_1}(\tau) \wp_{l, n_2} \rangle_{\text{stoch}}, \quad \tau > 0. \end{aligned}$$

For $\tau < 0$, swap the upper and lower rows of subscripts on the left hand side, as in Eq. (3.85). In the double entropy basis this is

$$\begin{aligned} \wp_{m_2, n_2}^{(2), SS}(\tau) &= \langle \mathcal{U}_{n_2, n_2}^S(\tau)^\dagger \mathcal{U}_{n_1, n_1}^S(\tau) \wp_{n_2, n_2}^S \rangle_{\text{stoch}} \\ &\quad \times \delta_{m_2, n_1} \delta_{m_1, n_2}, \quad \tau > 0. \end{aligned} \quad (3.94)$$

Recall that the probability operator and the time propagator are diagonal in the entropy representation.

As a check that the time propagator expression for the time correlation function is correct, the leading order terms in the small τ expansion of both sides of Eq. (3.94) will now be obtained explicitly. This is only done in the high temperature limit in which the expectation entropy and the actual entropy are the same. The right hand side

is

$$\begin{aligned} \text{RHS}_{m_2, n_2}^{SS} &= \frac{\delta_{m_2, n_1} \delta_{m_1, n_2}}{Z} \langle e^{S_{n_2, n_2}^S / k_B} \mathcal{U}_{n_2, n_2}^S(\tau)^\dagger \\ &\quad \times \mathcal{U}_{n_1, n_1}^S(\tau) \rangle_{\text{stoch}}, \quad \tau > 0. \end{aligned} \quad (3.95)$$

Now with $\hat{\lambda} \equiv \sum_n \lambda_n |\zeta_n^S\rangle \langle \zeta_n^S|$ and $\hat{\mathcal{R}} \equiv \sum_n r_n |\zeta_n^S\rangle \langle \zeta_n^S|$, the stochastic propagator is

$$\begin{aligned} \mathcal{U}_{m, n}^S(\tau) &= \left\{ \hat{I} + \frac{\tau}{i\hbar} \hat{\mathcal{H}} - \frac{|\tau|}{2T\bar{N}} \hat{\lambda} [\hat{\mathcal{H}} - E_0 \hat{I}] + \hat{\mathcal{R}} \right\}_{m, n}^S \\ &= \left\{ 1 + \frac{\tau}{i\hbar} E_n - \frac{|\tau|}{2T\bar{N}} \lambda_n [E_n - E_0] \right. \\ &\quad \left. + r_n \right\} \delta_{m, n}. \end{aligned} \quad (3.96)$$

Using this and the variance of the random operator, to linear order in the time step the right hand side of the transition probability, Eq. (3.94), is

$$\begin{aligned} \text{RHS}_{m_2, n_2}^{SS} &= \frac{\delta_{m_1, n_2} \delta_{m_2, n_1}}{Z} e^{S_{n_1, n_1}^S / k_B} \\ &\quad \times \left\{ 1 + \frac{\tau}{i\hbar} [E_{n_1} - E_{n_2}] \right. \\ &\quad \left. - \frac{|\tau|}{2T\bar{N}} (\lambda_{n_1} [E_{n_1} - E_0] + \lambda_{n_2} [E_{n_2} - E_0]) \right. \\ &\quad \left. + \frac{|\tau| \lambda_{n_1} [E_{n_1} - E_0]}{2T\bar{N}} \delta_{m_1, n_1} \right\}. \end{aligned} \quad (3.97)$$

The double diagonal part of this is

$$\text{RHS}_{m, m}^{SS} = \frac{1}{Z} e^{S_{m, m}^S / k_B}. \quad (3.98)$$

This is just the singlet probability. These diagonal terms are independent of the choice of the λ_n . For these the time correlation function is independent of the specific model of the reservoir interactions with the sub-system.

The non-diagonal terms are the ones that depend upon the time step, and this means that the time correlation function as a function of τ will depend upon the drag coefficients. However, since the reservoir should represent a weak perturbation of the sub-system (the boundary region should be much smaller than the sub-system itself), the magnitudes of the λ_n should be small enough that the irreversible term (the one proportional to $|\tau|$) should be dominated by the adiabatic, reversible term (the one proportional to τ).

In order to show that this is equal to the left hand side of Eq. (3.94), which are the coefficients of the transition probability matrix, the eigenfunctions of the second entropy operator are required. Recall that the domain is $\mathbb{H} \otimes \mathbb{H}$, and so one can invoke a basis of the form $\{|\zeta_{m_2}\rangle, |\zeta_{m_1}\rangle\}$. (One could normalize this by a factor of $\sqrt{2}$.) In quantum mechanics one can neglect an overall phase factor for the wave function. However in the

present case there is the possibility of a phase difference between the two Hilbert spaces and this should be considered. In particular the basis $\{-|\zeta_{m_2}\rangle, |\zeta_{m_1}\rangle\}$ differs from the first basis by a phase of π and spans a space orthogonal to that spanned by the first one. In the following analysis wave functions will be projected onto the sub-space spanned by the first basis on the grounds that it is the dominant one. The first reason for this is that the small time step limit is being considered, in which case the phase of ψ_2 must be almost the same as that of ψ_1 . The second reason is that it will be shown that the leading eigenfunction in the second basis is negative and diverges in the small time step limit. Because this appears in the exponent of the transition probability, it contributes negligibly to the transition.

The second entropy operator acting on a basis vector in the double entropy basis is

$$\begin{aligned} \hat{S}^{(2)}(\tau) \begin{pmatrix} |\zeta_{m_2}^S\rangle \\ |\zeta_{m_1}^S\rangle \end{pmatrix} \\ = 2\overline{N} \begin{pmatrix} \hat{a}(\tau) & \hat{b}(\tau) \\ \hat{b}(\tau)^\dagger & \hat{c}(\tau) \end{pmatrix} \begin{pmatrix} |\zeta_{m_2}^S\rangle \\ |\zeta_{m_1}^S\rangle \end{pmatrix} + \overline{S}^{(1)} \begin{pmatrix} |\zeta_{m_2}^S\rangle \\ |\zeta_{m_1}^S\rangle \end{pmatrix} \\ = 2\overline{N} \begin{pmatrix} \frac{-\hat{\lambda}^{-1}}{|\tau|} + \hat{a}_0 + \hat{\tau}a'_0 & \frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{b}_0 \\ \frac{\hat{\lambda}^{-1}}{|\tau|} + \hat{b}_0 & \frac{-\hat{\lambda}^{-1}}{|\tau|} + \hat{a}_0 - \hat{\tau}a'_0 \end{pmatrix} \begin{pmatrix} |\zeta_{m_2}^S\rangle \\ |\zeta_{m_1}^S\rangle \end{pmatrix} \\ + \overline{S}^{(1)} \begin{pmatrix} |\zeta_{m_2}^S\rangle \\ |\zeta_{m_1}^S\rangle \end{pmatrix} + \mathcal{O}(\tau). \end{aligned} \quad (3.99)$$

It is clear that to leading order the eigenfunction are of the form $|\zeta_m^S, \zeta_m^S\rangle$ with eigenvalue $\overline{S}^{(1)}$, and $|\zeta_m^S, \zeta_m^S\rangle$ with eigenvalue $-4\overline{N}\lambda_m^{-1}/|\tau|$. The latter is large and negative in the small time step limit, and eigenfunctions of this form can be neglected.

One needs to go to the first correction to the leading eigenvalue in order to obtain its dependence on the modes. The next order eigenfunction has the form

$$\begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \tau \begin{pmatrix} -\hat{\beta}|\zeta_m^S\rangle \\ \hat{\beta}|\zeta_m^S\rangle \end{pmatrix} + |\tau| \begin{pmatrix} -\hat{\gamma}|\zeta_m^S\rangle \\ \hat{\gamma}|\zeta_m^S\rangle \end{pmatrix}. \quad (3.100)$$

With this the second order term, $\mathcal{O}(\tau^0)$, for the right hand side of the eigenfunction equation is

$$\begin{aligned} \text{RHS} &= 4\overline{N} \begin{pmatrix} (\hat{\tau}\hat{\beta} + \hat{\gamma})\hat{\lambda}^{-1}|\zeta_m^S\rangle \\ -(\hat{\tau}\hat{\beta} + \hat{\gamma})\hat{\lambda}^{-1}|\zeta_m^S\rangle \end{pmatrix} + \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} \\ &+ 2\overline{N} \begin{pmatrix} (\hat{a}_0 + \hat{b}_0 + \hat{\tau}a'_0)|\zeta_m^S\rangle \\ (\hat{a}_0 + \hat{b}_0 - \hat{\tau}a'_0)|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \end{aligned} \quad (3.101)$$

In order for this to be an eigenfunction, $\hat{\gamma}$ must equal zero. The coefficient $\hat{\tau} \equiv \text{sign } \tau$ vanishes when

$$\hat{\beta} = \frac{-1}{2}\hat{a}'_0\hat{\lambda}. \quad (3.102)$$

One now has, to the two leading orders,

$$\text{RHS} = \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + 2\overline{N} \begin{pmatrix} (\hat{a}_0 + \hat{b}_0)|\zeta_m^S\rangle \\ (\hat{a}_0 + \hat{b}_0)|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau)$$

$$\begin{aligned} &= \overline{S}^{(1)} \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \overline{N} \begin{pmatrix} \hat{S}''|\zeta_m^S\rangle \\ \hat{S}''|\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau) \\ &= \left[\overline{S}^{(1)} - \frac{E_m - E_0}{T} \right] \begin{pmatrix} |\zeta_m^S\rangle \\ |\zeta_m^S\rangle \end{pmatrix} + \mathcal{O}(\tau). \end{aligned} \quad (3.103)$$

The the m -dependent part of the prefactor is the relevant eigenvalue, $S_{mm}^S = -E_m/T$, the constant remainder being incorporated into the the normalizing partition function $Z^{(2)}(\tau)$. Hence the double diagonal part of the left hand side of Eq. (3.94) is

$$\begin{aligned} \phi_{m,m}^{(2),SS}(\tau) &= \frac{1}{Z^{(2)}(\tau)} \langle \zeta_m^S, \zeta_m^S | e^{\hat{S}^{(2)}/k_B} | \zeta_m^S, \zeta_m^S \rangle \\ &= \frac{1}{Z'^{(2)}(\tau)} e^{S_{mm}^S/k_B}. \end{aligned} \quad (3.104)$$

One sees that this is equal to the right hand side, Eq. (3.98), which validates the propagator expression for the time correlation function, Eq. (3.88). It is not possible to carry out the check to $\mathcal{O}(\tau)$ because the expansion for the second entropy is only valid to $\mathcal{O}(\tau^0)$.

3. Parity

Operators that represent physical observables are Hermitian, $\hat{A} = \hat{A}^\dagger$. Without loss of generality they may be taken to be either real or imaginary, since, if complex, they can be split into their real and imaginary parts. Let $\epsilon_A = \pm 1$ denote the parity of the operator, $\hat{A} = \epsilon_A \hat{A}^* = \epsilon_A \hat{A}^T$, and similarly for other operators.

The expectation value in the wave state ψ is

$$A(\psi) = \frac{\underline{\underline{A}} : \underline{\underline{\psi}} \underline{\underline{\psi}}^*}{\underline{\underline{\psi}}^* \cdot \underline{\underline{\psi}}}, \quad (3.105)$$

and that in the wave state ψ^* is

$$A(\psi^*) = \frac{\underline{\underline{A}} : \underline{\underline{\psi}}^* \underline{\underline{\psi}}}{\underline{\underline{\psi}}^* \cdot \underline{\underline{\psi}}^*} = \frac{\underline{\underline{A}}^T : \underline{\underline{\psi}} \underline{\underline{\psi}}^*}{\underline{\underline{\psi}}^* \cdot \underline{\underline{\psi}}} = \epsilon_A A(\psi). \quad (3.106)$$

Since conjugation of the wave state represents velocity reversal, one sees from this that the parity of an operator signifies whether it is even or odd under time reversal.

Since Hermitian operator have real expectation values, $C_{BA}(0)$ is real if, and only if, $\hat{B}\hat{A}$ is Hermitian. Since the two operators are individually Hermitian, this implies that they must commute,

$$C_{BA}(0)^* = C_{BA}(0) \Leftrightarrow \hat{B}\hat{A} = \hat{A}\hat{B}. \quad (3.107)$$

In this case $C_{BA}(0^+) = C_{BA}(0^-)$.

Explicitly one has

$$\begin{aligned} C_{BA}(0^+)^* &= \langle \hat{B}\hat{A} \rangle_{\text{stat}}^* \\ &= \int d\psi \frac{\langle \psi | \hat{B}\hat{A} | \psi \rangle^*}{\langle \psi | \psi \rangle^*} \\ &= \int d\psi \frac{1}{N(\psi)} \underline{\underline{\psi}} \cdot \underline{\underline{\psi}}^* \cdot \underline{\underline{B}}^* \cdot \underline{\underline{A}}^* \cdot \underline{\underline{\psi}}^* \end{aligned}$$

$$\begin{aligned}
&= \epsilon_A \epsilon_B \int d\psi^* \frac{1}{N(\psi)} \underline{\psi}^* \cdot \underline{\mathcal{Q}} \cdot \underline{B} \cdot \underline{A} \cdot \underline{\psi} \\
&= \epsilon_A \epsilon_B C_{BA}(0^+). \tag{3.108}
\end{aligned}$$

The final equality follows because the integral is over all of Hilbert space, and so $\underline{\psi}^*$ is a dummy variable of integration. Since the time correlation function is real if the operators commute, this proves that

$$\langle \hat{B}(0) \hat{A}(0) \rangle_{\text{stat}} = 0 \text{ if } \epsilon_A \neq \epsilon_B \text{ and } \hat{B} \hat{A} = \hat{A} \hat{B}. \tag{3.109}$$

In other words, commuting operators with opposite parity are instantaneously uncorrelated. If the operators do not commute and have opposite parity, then the time correlation function at $\tau = 0$ is imaginary, $C_{BA}(0^+)^* = -C_{BA}(0^+)$. Hence one can say that in general $\text{Re } C_{BA}(0) = 0$ if $\epsilon_A \neq \epsilon_B$.

From the symmetry conditions for the second entropy given in §III B 1, one sees that the complex conjugate of the transition probability operator has the symmetry

$$\hat{\phi}^{(2)}(\tau)^* = \hat{\phi}^{(2)}(-\tau). \tag{3.110}$$

Accordingly

$$C_{BA}(\tau)^* = \text{Tr}^{(2)} \hat{\phi}^{(2)}(\tau)^* \{ \hat{B}^*, \hat{A}^* \}$$

$$\begin{aligned}
&= \epsilon_A \epsilon_B \text{Tr}^{(2)} \hat{\phi}^{(2)}(-\tau) \{ \hat{B}, \hat{A} \} \\
&= \epsilon_A \epsilon_B C_{BA}(-\tau). \tag{3.111}
\end{aligned}$$

If \hat{A} and $\hat{B}(\tau)$ commute, then their time correlation function is real, $C_{BA}(\tau)^* = C_{BA}(\tau)$. In this case

$$C_{BA}(\tau) = \epsilon_A \epsilon_B C_{BA}(-\tau) = \epsilon_A \epsilon_B C_{AB}(\tau). \tag{3.112}$$

This may also be seen from the propagator expression, Eq. (3.88). Noting that $\hat{U}(\tau)^* = \hat{U}(-\tau)$, and assuming that the time correlation function is real, one has

$$\begin{aligned}
C_{BA}(\tau) &= C_{BA}(\tau)^* \\
&= \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B} \hat{U}(\tau) \hat{A} \hat{\phi} \rangle_{\text{stoch}}^* \\
&= \text{Tr}^{(1)} \langle \hat{U}(\tau)^\dagger \hat{B}^* \hat{U}(\tau)^* \hat{A}^* \hat{\phi}^* \rangle_{\text{stoch}} \\
&= \epsilon_A \epsilon_B \text{Tr}^{(1)} \langle \hat{U}(-\tau)^\dagger \hat{B} \hat{U}(-\tau) \hat{A} \hat{\phi} \rangle_{\text{stoch}} \\
&= \epsilon_A \epsilon_B C_{BA}(-\tau). \tag{3.113}
\end{aligned}$$

This result is the analogue of the classical result given in §2.5.1 of Ref. 2.

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